MODIFICATION OF AMINE COLLECTORS FOR LOW TEMPERATURE FLOTATION OF POTASH

A Thesis Submitted to the College of Graduate Studies and Research

In Partial Fulfillment of the Requirements

For the Degree of Master of Science

In the Department of Mechanical Engineering

University of Saskatchewan

Saskatoon

By

EBENEZER ESSILFIE

PERMISSION TO USE

In presenting this thesis/dissertation in partial fulfillment of the requirements for a Postgraduate degree from the University of Saskatchewan, I agree that the Libraries of this University may make it freely available for inspection. I further agree that permission for copying of this thesis/dissertation in any manner, in whole or in part, for scholarly purposes may be granted by the professor or professors who supervised my thesis/dissertation work or, in their absence, by the Head of the Department or the Dean of the College in which my thesis work was done. It is understood that any copying or publication or use of this thesis/dissertation or parts thereof for financial gain shall not be allowed without my written permission. It is also understood that due recognition shall be given to me and to the University of Saskatchewan in any scholarly use which may be made of any material in my thesis/dissertation.

DISCLAIMER

Reference in this thesis/dissertation to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not constitute or imply its endorsement, recommendation, or favoring by the University of Saskatchewan. The views and opinions of the author expressed herein do not state or reflect those of the University of Saskatchewan, and shall not be used for advertising or product endorsement purposes.

Requests for permission to copy or to make other uses of materials in this thesis/dissertation in whole or part should be addressed to:

Head of the Department of Mechanical Engineering

University of Saskatchewan

Saskatoon, Saskatchewan S7N 5A9

Canada

OR

Dean

College of Graduate Studies and Research

University of Saskatchewan

107 Administration Place

Saskatoon, Saskatchewan S7N 5A2

Canada .

ABSTRACT

The most common potash ore in Canada is sylvinite which consists of mainly halite (NaCl) and sylvite (KCl) with addition of trace amounts of insoluble materials such as clay and silt. KCl is loosely referred to as potash or sylvite and NaCl as salt or halite. The potash (KCl) is separated from NaCl for the production of fertilizer for agricultural use and other industrial applications. KCl is separated from NaCl mainly by a flotation process. The most common collector (flotation reagent) used in the flotation process are long chain aliphatic amines. Temperature variations have adverse effect on the physical, chemical and physicochemical properties of amine dispersion, viscosity of the brine solution, dissolution and adsorption of the amine as well as the wettability of the potash particles. The froth flotation process is efficient when temperatures are within the range of 20^{o}C-32^{o}C. Inefficiency of the flotation process occurs when temperature of the saturated brine falls below 15^{o}C because of the inability of amine collectors to disperse well in highly viscous brines. The primary purpose of this study was to select organic additives that can improve the rate of dispersion of the collector emulsion and enhance recovery of KCl from lower temperature (10-15^{o}C) brine solutions. The secondary goal was to determine the optimum particle size of potash required for low temperature flotation.

Particle size distributions of amine precipitates were determined using a Malvern Mastersizer S Long Bench Particle Size Analyzer. Dispersion experiments were performed and optical (OM) and scanning electron microscopy techniques (SEM) were used to determine the effect of selected additives on dispersion of amine particles in saturated brine solutions. Based on results from the dispersion tests, the most effective additive, polyglycol ether (PGE) was selected and mixed with dodecyl amine-hydrochloride to form a modified amine collector. Flotation experiments were carried out in saturated brines at lower temperatures (10- 15^{o}C) and higher temperatures (24-28^{o}C) to determine the effect of the presence of additives on flotation recovery. Urea was added to the brine solution to determine its impact on recovery.

Flotation with the modified collector led to 12% increase in flotation recovery at 10-15^{o}C. The flotation recovery further increased by 1.9% when urea was added to the saturated brine prior to flotation. It was discovered that the modified collector functioned as a collector and as frother and additional frother was not required for the flotation process. The optimum particle size of potash required for improved flotation with the modified collector was 180-335µm.

ACKNOWLEDGEMENT

First and foremost I would like to thank God for the strength, grace and wisdom He gave me to complete my MSc program. My sincere thanks go to my supervisors, Dr. Jerzy Szpunar and Dr. Ajay Dalai for all their support and guidance. Without them I could not have finished this project. I appreciate the funding, their efforts and dedication.

My special thanks go to my advisory committee members, Dr. Ikechukwuka Oguocha and Dr. Gabriel Akindele Odeshi, whose guidance, patience and help I am extremely grateful for. They were there for me all the time. I cannot forget Dr. John Adjaye of Syncrude Canada Limited who guided and provided mentorship as to how to go about some of the experiments carried out in this project.

I am also thankful to Valerie Mckenzie and Richard Blondin for their help in doing the adsorption test and the dispersion tests.

To my parents, my friends and my relations in Canada, the Adjaye Deheer family, for the love and encouragement given me throughout my studies, I say a big thank you.

Many thanks go to Dr. Rambabu Nedunuri, and Cathlene Jacobson of Mosaic Comapany, Canada, for their insightful discussions and comments about my work and for offering their support whenever I needed it. I say a very big thank you to every one of you. I am grateful.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

DDA-HCl	Dodecylamine hydrochloride
HDA-HCl	Hexadecylamine hydrochloride
MIBC	Methyl isobutyl carbinol
ODA-HCl	Octadecylamine hydrochloride
PGE	Polyglycol ether
SEM	Scanning electron microscope
XRD	X-ray diffractometer
XPS	X-ray photospectroscopy

1. INTRODUCTION

1.1 Overview

Potash is one of the world's most important minerals and it is used in agricultural and other industrial processes. The most common potash ore in Canada is sylvinite which is made up of halite (NaCl) and sylvite (KCl). KCl may loosely be referred to as potash whereas NaCl may be referred to as salt. The potash is primarily comprised of potassium which is one of the three main plant nutrients that make up fertilizer, along with nitrogen and phosphate. There is no substitute for potassium compounds in agriculture; they are essential to maintain and expand food production. Potassium is therefore referred to as 'the regulator' because it is used to regulate essential processes such as; enzyme activation, photosynthesis, water use efficiency, starch formation and protein synthesis (Garrett, 1997).

Potash is extracted from two main sources: i) buried ancient evaporites and ii) brine formed from landlocked water bodies, such as the Dead Sea (Israel), Salar de Atacama (Chile) or Great Salt Lake (U.S.A). Canada is the largest producer and exporter of potash and the province of Saskatchewan has one of the largest potash deposits in the world. Potash is mined by two different methods depending on the source of the ore. If the potash ore is sourced from ancient buried evaporite, the conventional shaft mining (underground mining) is usually employed. On the other hand if the source of the ore is landlocked water bodies then solution mining is employed. Underground mining is type of mining method where the ore body located underground is accessed by shafts, dug out and transported to the surface for processing. Solution mining on the other hand is where a hole is drilled to meet the ore body, water is injected to dissolve the ore and then the solution is pumped out for processing. Both methods require separation of the potash from the salt when the raw material is transported to the surface. Conventional shaft mining normally uses flotation and heavy media separation techniques while the solution mining employs evaporation of the water and crystallization of the potash.

Once transported to the surface, Potash is recovered by three major processes, namely flotation, crystallization and electrostatic separation. About 70% of the total potash is produced by conventional froth flotation (Perucca, 2003). Froth flotation is the process by which the mineral

component of interest is separated from the other components of the mineral ore with the help of air bubbles and chemicals known as flotation reagents. Crystallization process is used when the ore is in the form of a solution so that an external force is applied to solidify or crystallize out the valuable components of the mineral. It may also be used as an extension to flotation in some plants to help improve the grade of the final product and increase recovery. There are two types of the crystallization process; Mechanical crystallization and natural crystallization. In Mechanical crystallization, the potash ore is mixed with hot water (100-110^{o}C) and agitated to selectively dissolve sylvite ahead of halite. The dissolved sylvite (brine liquor) is cooled down to about 20 °C to obtain KCl crystals by differential crystallization. The undissolved sodium chloride and insoluble content of the potash ore are then removed in a clarifier. In natural crystallization, KCl is produced from naturally occurring brines from the Dead Sea, the Great Salt Lake or from the Salar de Atacama by transporting brine into evaporations pans and allowing the water in the brine to evaporate leaving a concentrated brine in the pan. Most of the NaCl crystallizes out after evaporation. The concentrated brine is then pumped into a second series of open pans, where sylvite settles naturally at the bottom of the pan.

The third separation method, electrostatic separation, is scarcely used. In this process the salt at a relative humidity of 2-30% is electrically charged. It is conditioned with a chemical agent and is made to pass through an electrostatic field to separate the crude salt into at least two fractions and to separate the utilized conditioning agent (US patent number 4276154A, 1981).

Canada produces the highest quantity of potash in the world. It was recorded in 2012, that 26.5% of the world's potash was produced from Canada (Potash Corporation of Saskatchewan Inc., 2013). In Saskatchewan alone, there are about ten potash mines in operation. The major producers of potash in Canada are International Mineral Corporation (IMC), Potash Corporation

One of the major problems that affect mineral processing is variations in temperature (Wilson et al., 1969; O'Connor et al., 1984; Lin, 1988; Trent et al., 2010). In the province of Saskatchewan where majority of the potash mines are located, temperatures can change from Summer (28-30^{o}C) to Winter (10-15^{o}C) and from daytime (28-30^{o}C) to nighttime (15-18^{o}C), affecting the efficiency of the potash processing units. In potash flotation, variations in temperature influence the choice of flotation reagents (especially amine collectors) with regards to the degree of saturation. When temperature of the brine rises above 32^{o}C, the amine used must have a higher

degree of saturation in order to maintain its effectiveness. Lower temperatures (10-15^{o}C) require unsaturated amines. Thus, low recovery problems associated with a drop in temperature can be corrected by replacing the amine collector with a more unsaturated aliphatic amine which is usually required for low temperature flotation. However, switching collectors as temperature condition changes, can also affect production since operating parameters and process conditions must be altered to suit the new collector. This slows down the whole process. Besides, it is possible for the temperature of the saturated brine to significantly change over a short period of time (from day to night) in which case switching collectors becomes almost impossible. The aim of this research is to use organic additives to modify amine collectors in order to maintain their effectiveness at lower temperature conditions (10-15^{o}C). This will ensure the use of flotation collectors during winter and summer.

1.2 Motivation (Knowledge Gap)

Most of the research work done in this area was focused on normal temperatures (20-30^{o}C) (Monte and Oliveira, 2004; Qinbo et al, 2010 and Burdukova et al, 2009) and not at low temperatures (10-15 ^{o}C). Long chain primary amines (amine collectors) have been successfully used to efficiently float potash from saturated brine (Tippin, 1998; Berton et al., 1971) but little information on the effect of temperature on amine dispersion is available. Meanwhile, the effectiveness of amine collectors for selective flotation of KCl depends primarily on the temperature of the saturated brine. If the temperature of the saturated brine is high, the amine must have a high degree of saturation (characterized by a high iodine value) to maintain its stability. On the other hand, if the temperature of the brine is low the amine must have a high degree of unsaturation for the flotation to maintain its efficiency as a collector. The long chain primary amines that are used in potash flotation are saturated amines because they are used at temperatures between 20^{o}C to 32^{o}C regarded as high temperatures. The major effect of low temperature on amine efficiency is poor dispersion of the amine aggregates in saturated brine.
In this work some selected additives (urea and several types of alcohols used in potash flotation) were evaluated to determine their effect on amine dispersion.

1.3 Objectives

The objectives of this research were;

1. To determine the effect of the temperature on size and morphology of amine precipitates.
2. To determine the effect of selected additives on dispersion of amine and viscosity of the brine solution.
3. To select the best additive for modification of the amine collector and to determine the effect of the modified amine on flotation recovery
4. To determine the optimum particle size of potash for improved recovery of potash.

1.4 Thesis Outline

Chapter 2 is a literature review on potash processing and the various parameters employed in the flotation process, outlining the various process units, the flotation reagents, and the mechanism of the flotation process. This chapter also introduces the theories of froth flotation, effect of temperature on flotation and effect of additives on amine dispersion. Chapter 3 highlights the materials and the experimental procedure. It gives an overview of the experiments that were carried out and the materials and equipment that were used to achieve the objectives. Chapter 4 discusses the findings and interpretation of the results. Chapter 5 consists of the summary of the outcome of this research, the conclusions and recommendations for future studies and chapter 6 gives the references used in this thesis.

2. LITERATURE REVIEW

2.1. Potash mining in Saskatchewan

In 1943, exploration geologists were drilling for oil when potash was accidentally discovered for the very first time in Saskatchewan. The huge deposit stretched from the southern plains of Saskatchewan through Rocanville, Esterhazy and Saskatoon. The deposit continues to a depth of about 1,600 meters at Belle Plaine and up to a depth of about 3,000 meters in Northeastern Montana and North Dakota. (Saskatchewan Mining Association, 2013). In 1962, after going through challenges and delays in overcoming underground water and shaft sinking problems, the mining of potash started fully in Saskatchewan, having the world's first solution mine. By the year 1971, Saskatchewan had ten operating potash mines, making Saskatchewan one of the largest producers of potash in the world (Saskatchewan Geological Society and North Dakota Geological Society, 2010) Currently, Canada is the world's largest producer and exporter of potash having about 46% of the world's potash reserves found in the Saskatchewan province within the Prairie Evaporite Deposit (Natural Resources Canada, 2012). Figure 2.1 shows a map of the Saskatchewan potash reserve.

In 2012, over $7.9bn in revenue was generated from potash mining in Saskatchewan (Potash Corporation of Saskatchewan Inc. 2013). Revenue generated from potash mining is used to help support the governments' projects through the payment of taxes and royalties. Potash mining has provided employment to a large group of people.

In a recent article published by D'Arcy Jenis, the Mosaic Company and Agrium Inc. are investing $14 billion in mine expansions and there is a German based company, K+S currently developing the first new potash mine in Saskatchewan in 40 years at a cost of $4.1 billion and scheduled to produce the first ton of potash in 2016. The giant Australia's BHP Billiton and Vale Potash Canada Ltd. also have major new potash mines underway in Regina.

2.2. Processing

The major process used in processing potash is the flotation process. Before flotation, the potash ore undergoes some important stages that have been duly reviewed by Carlos Perucca (2003) and briefly reviewed in this thesis. Figure 2.2 summarizes the various stages the potash ore goes through to obtain the finished product. The medium for separation of potash from the ore is brine

solution. The brine solution should be saturated in order to keep potash solid in solution. The brine is usually made up of NaCl and KCl. Table 2.1 represents properties of potassium sodium chloride solutions.

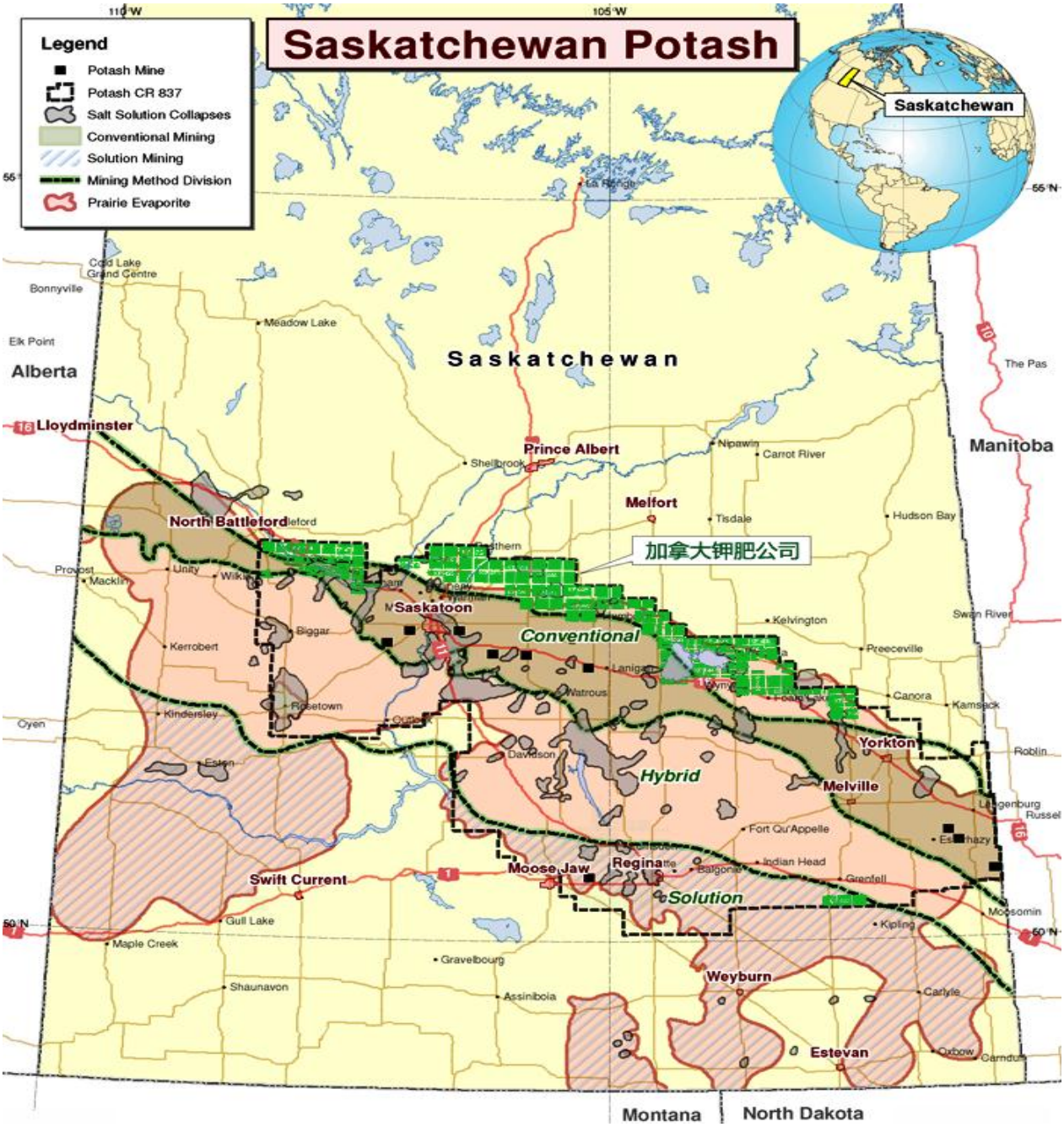


Figure 2.1. The Saskatchewan Potash (www.canadapotash.com; Canada Potash Corporation, 2012).

Table 2.1. Properties of Potassium Sodium Chloride Solutions

% KCl	Density(kg/ m3)	KCl(kg/m3)	KCl(mg/L)	K+(mg/L)	Cl-(mg/L)	Final Volume Factor
1	1006	11.4	10050	5271	4779	1.004
2	1013	20.0	20220	10605	9615	1.008
4	1026	39.9	40960	21482	19478	1.016
6	1039	62.8	62210	32627	29583	1.024
8	1052	82.8	84000	44056	39945	1.033
10	1065	105.6	106300	55752	50548	1.043
12	1079	128.4	129200	67762	61439	1.053
14	1093	154.1	152700	80087	72613	1.064
16	1106	176.9	176700	92674	84026	1.076
18	1120	202.6	201300	105576	95724	1.088
20	1135	225.4	226600	118845	107755	1.102
22	1149	251.1	252400	132376	120024	1.115
24	1160	279.6	279000	146327	132673	1.028

Properties based on 20°C and 100% purity

2.2.1. Crushing/Milling

The particle size of the ore required for flotation is usually below 2 mm. The run-of-mine ore, (the potash ore excavated from underground or crystallized product from solution mining transported to surface) however come in sizes of about 150mm to 200mm from underground and therefore must be reduced to smaller sizes. Particle size reduction is achieved by crushing, where heavy duty crushers are used to break the ore down. The required size is not achieved in one crushing stage. The ore goes through about three stages of size reduction. There are primary, secondary and tertiary crushers that help to achieve maximum particle size reduction. Some mines incorporate a milling stage after the crushing stage to accomplish a particle reduction to a size amenable for floatation. The process of breaking the particle size of the run-of-mine ore by crushing or milling is known as comminution. The purpose of communition is to liberate as much KCl as possible from NaCl and the other impure components of the ore. The objective of this process is to selectively separate KCl from NaCl. Comminution also helps in the easy transportation of the ore from one processing unit to the next. (Perucca, 2003 and Kawatra, 2001).

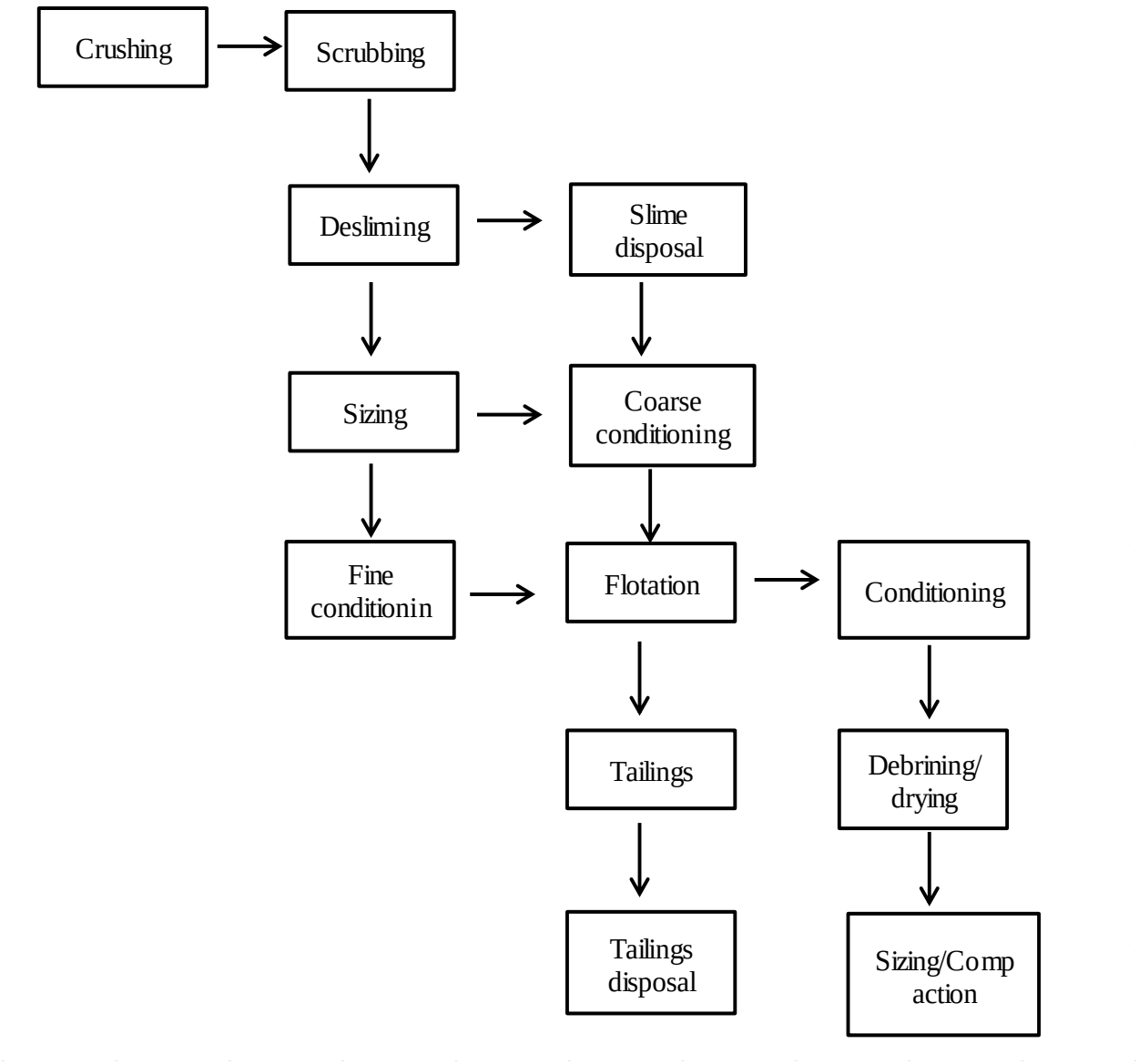


Figure 2. 2 Schematic block diagram of a conventional potash flotation plant (Perucca, 2003).

2.2.2. Scrubbing and desliming

All insoluble matter must be removed prior to flotation to make the process efficient. This is achieved by washing the ore with enough KCl-NaCl saturated solution under strong agitation. Saturated solution is used instead of fresh water so that the potash stays in solution without losing the valuable component via dissolution.

2.2.3. Slime disposal and sizing

The tailings from the scrubbing and desliming units are dumped in tailings dam and the deslimed slurry goes through a separation unit where wet screening or any hydro-separation mechanism is used to separate the ore into fine and coarse materials. This ensures separate conditioning for the fine and coarse potash particles to optimize reagent consumption.

2.2.4. Flotation

The flotation process is normally carried out in series (multiple stages). Some of the tailings that are suspected to contain a reasonable quantity of KCl (high tailings grade) may be recycled/recirculated. Recirculated feed are usually coarse and are often re-grinded and fed together with a fresh potash feed prior to floatation. Figure 2.3 shows a schematic flotation process. Flotation takes place in circuits called flotation cells. Inside the flotation cell is an agitator, saturated brine, potash particles and air bubbles. Flotation reagents (depressants, collectors and frothers) are used to ensure selective flotation of KCl from the potash ore

2.2.5. Flotation process.

The amine collector is then added to form a hydrophobic layer on the surface of potash particles or to spread on the air-liquid interface to enhance bubble-particle attachment and bring about flotation. The amine collectors are selective towards KCl so KCl particles become hydrophobic (floatable) due to the action of the collector molecules whiles NaCl becomes hydrophilic and stays in solution. Air is introduced into the cell to form bubbles which are needed to carry the activated potash particles to the surface to form froth. The function of the agitator is to stir the slurry to prevent the potash particles from settling at the bottom of the cell and to promote particle bubble attachment. The stirring rate of the agitator should be slow enough to prevent the potash particles from settling and as high as possible to prevent the bubbles from breaking up.

In the flotation system, depressants are added first followed by the collector reagents. The function of the depressant is to blind the surface of clay particles to prevent the adsorption of collector molecules when the collector is added. Otherwise they can float with KCl and affect the quality of the flotation concentrate (product). Collector molecules form a layer on the surface of the mineral rendering the mineral hydrophobic (the ability to float). The frother is the reagent that is added last. Most frothers used in potash processing are alcohols. The function of the

frother is to help reduce surface tension of the slurry in order to allow free movement of froth to the surface and also to help stabilize the froth and prevent it from breaking up. When bubbles break up, attached potash particles fall back into solution (Wills, 2006; Bulatovic, 2007).

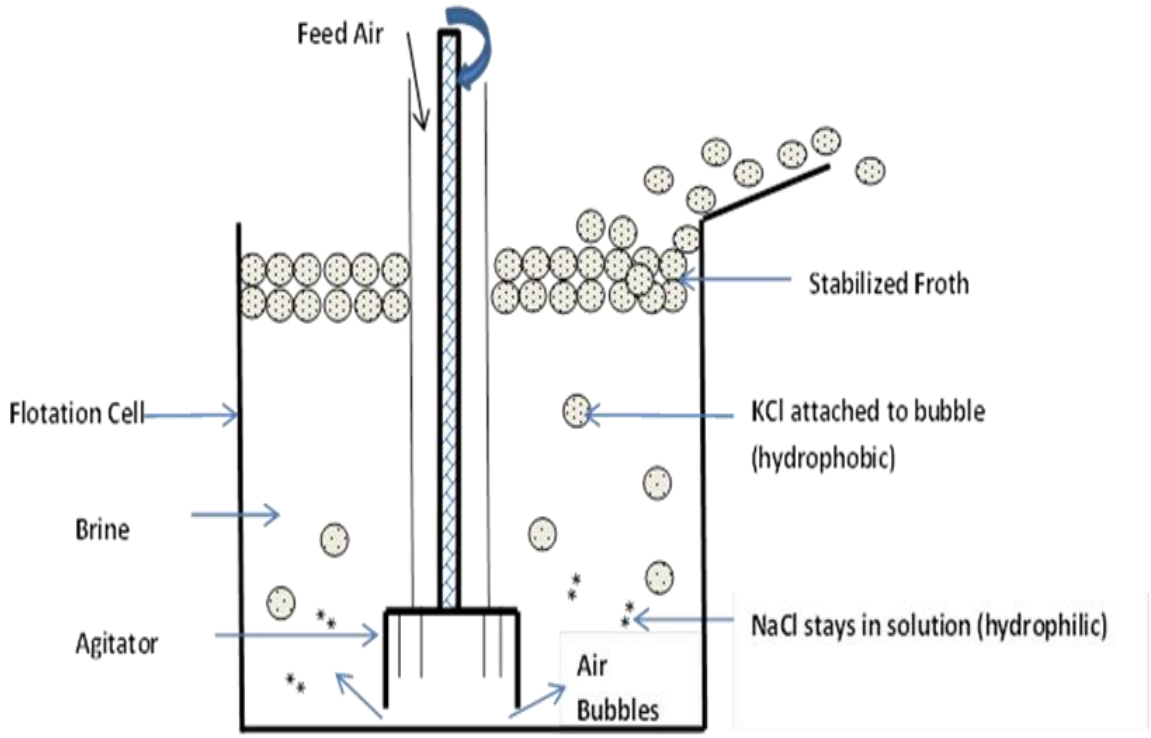


Figure 2. 3 Flotation process.

2.2.6. Debrining and tailings disposal

This is the stage where the mixture of flotation reagent and the brine are washed off the KCl particles. The solution containing a mixture of flotation reagents and saturated brine is recycled back into the flotation stream. The NaCl, clay and the other insoluble matter form the tailings and are disposed into the tailings dam.

2.2.7. Sizing of potash particles

Sizing is the final stage of potash processing where the KCl is separated into various sizes. The very fine particles are compacted into different sizes to form the final product. They are usually compacted into four different size ranges; fine, coarse, standard and granular. The market value of the potash is based on the size and chemical composition of the final product.

2.3. Hydrophobicity and particle-bubble attachment

One of the key factors that can affect the efficiency of flotation is the ability of the potash particles to get attached to air bubbles. As a matter of fact, flotation will not take place if there is no strong particle-bubble attachment. Before a potash particle can get attached to an air bubble, the surface of the particle must be conditioned for attachment. Thus, the particle must be converted from a hydrophilic (water-loving) state to hydrophobic (water-repellent) or aerophilic (air-loving) state. Some collectors such as amines and sulfonates can be used to effect this conversion by virtue of the electrostatic attraction between the polar head of the collector and the charged surface site of the mineral (Ozdemir et al., 2011; Bulatovic, 2007; Agar, 1990). This can be explained by the surface charge model. The polar side of the amine collector gets attracted to the negatively charged surface of the mineral (KCl) while the tail of the amine collector (the non-polar side) is directed upwards from the bulk solution in a manner as if to pull the mineral upwards. Thus the mineral becomes aerophilic (air-loving) making it easy to get attached to the air bubble for transportation to the froth phase. The amine molecular film stays at the interface of the mineral and bubble, acting as an adhesive. This is how hydrophobicity is imparted on the mineral particle.

However, the way the surface of a mineral is made hydrophobic or aerophilic is different for different minerals. In the flotation of silicates, the hydration of the mineral surface is responsible for hydrophobicity (Bulatovic, 2007; Laskowski and Kitchener, 1969). In the case of oxide minerals hydrophobicity is influenced by the electrochemical nature of the oxide-solution interface. According to Bulatovic, when hydrogen and hydroxyl ions adsorb on the surface of the oxide mineral, a polarizeable hydration layer with hydrogen-bonded structure forms (Bulatovic, 2007).

In the flotation of sulfide minerals hydrophobicity is imparted on a mineral by chemisorption of collector molecules onto the surface of the mineral. Molybdenum, elemental sulfur, realgar, graphite, diamond and talc are naturally hydrophobic. In the flotation of minerals, the ability of one mineral to float ahead of another mineral is due to the degree of hydrophobicity or wettability. In potash flotation, KCl is more hydrophobic than NaCl and therefore floats ahead of NaCl. Among KCl particles, the one that is highly hydrophobic floats, leaving the less

hydrophobic ones in solution. The difference in hydrophobicity is determined by the contact angle between the mineral particle and the bubble.

2.3.1. Contact angle measurement

The basis of flotation is the difference in the hydrophobicity of different minerals or components of a mineral. The measure of hydrophobicity is determined by the size of the contact angle. Thus, it is not just enough for particles to get attached to bubbles. The particle-bubble attachment must be strong enough to successfully carry the particle to the froth phase and not fall back into solution. It is therefore important that the contact angle of a bubble on a mineral particle should be known prior to using any collector. In measuring contact angle, the surface of the mineral is made clean and smooth, placed in distilled water and a bubble of air is pressed down from the bottom of a capillary tube. The absence of adhesion of the bubble on the surface confirms that the surface of the mineral is clean. The collector is then spread on the surface of the mineral and a bubble is placed on the surface to make an angle with the surface. The size of the contact angle made is a measure of floatability of the mineral (Bulatovic, 2007; Laskowski, 1986; Ralston and Neuxombe, 1992). As bubbles adhere onto mineral surfaces, tensile forces existing between the mineral and the bubble tend to separate them. The impact of the tensile forces leads to development of an angle (contact angle) between the mineral surface and the bubble (Bulatovic, 2007) as seen in Figure 2.4.

Bulatovic gave a simple mathematical expression relating the contact angle to surface energy,

$$W(s/a) = \Upsilon(s/l)\cos\theta \tag{2.1}$$

where $\Upsilon(s/a)$ represents the surface energies between solid and air, $\Upsilon(s/l)$ represents the surface energies between solid and liquid. Θ is the contact angle. The force required to break the particle-bubble interface is called the work of adhesion, $W(s/a)$. Thus, $W(s/a)$ is the force required to separate the solid air interface into separate air-liquid interface and solid liquid interface. $\Upsilon(l/a)$ in (2.2) represents the surface energies between liquid and air.

Given

$$W(s/a) = \Upsilon(l/a) + \Upsilon(s/l) - \Upsilon(s/a) \tag{2.2}$$

It implies that

$$W(s/a) = \Upsilon l/a\,(1 - \cos\theta) \qquad (2.3)$$

From equation (2.3), it implies that the larger the contact angle Θ, the greater the work of adhesion between particle and bubble, $W(s/a)$ and, therefore, the greater the chances of successful flotation of particles.

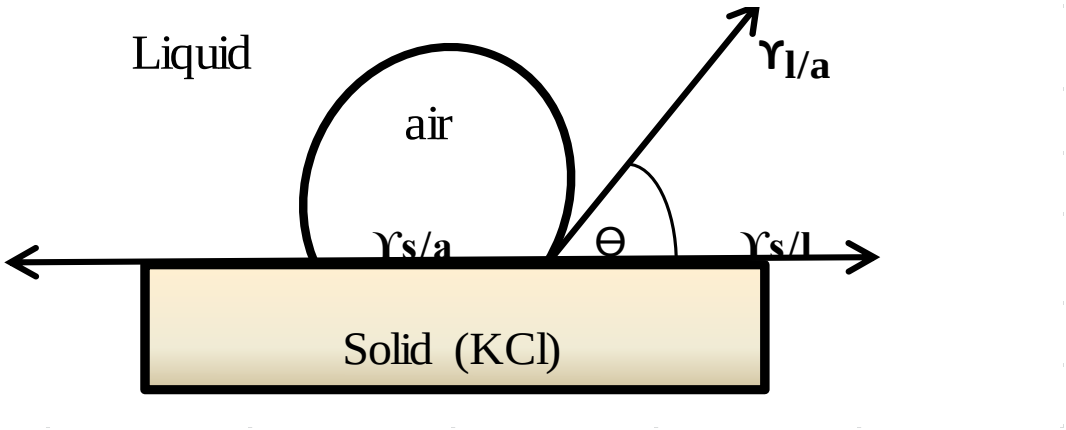


Figure 2. 4 Contact angle between bubble and mineral particle.

In a recent paper published by Laskowski (2013), he explained that in the potash flotation process, not only does the amine molecular film adhere to the surface of the potash particle to make them hydrophobic, the amine film can also spread on the surface of air bubbles such that potash particles can be picked up and transported to the surface. He observed that when amine dispersion was placed on a KCl surface, the KCl was not very hydrophobic and the contact angle was about 40^o. On the other hand, when amine was deposited onto bubbles, the measured contact angles were as high as 50^o-60^o, indicating a higher hydrophobicity.

Non-ionizing collectors are made up mainly of hydrocarbon compounds. They are non-polar and therefore, not soluble in water. They are usually liquid, non-polar hydrocarbons of various structures. Their potential is in their strong affinity for minerals that are hydrophobic to some extent. They are usually fuel oils and kerosene and they function by increasing the hydrophobicity of the selected mineral. Non-ionic collectors find application in the floatation of naturally hydrophobic minerals such as coal, molybdenite, talc and elemental sulfur. The effectiveness of non-ionic collectors like fuel oil and kerosene lie in the fact that they have a very low viscosity and can easily disperse in the slurry or pulp and spread over surfaces of mineral particles to cause particle-bubble attachment to take place. In some flotation systems they are

used as ‘extender oils’ to condition coarser mineral particles. Ionizing collectors are classified into two groups; Anionic collectors and Cationic collectors.

2.3.2 Dynamic light scattering

Amine collectors used in potash flotation are not soluble in saturated brine. When they are added to the flotation system, they form aggregates/precipitates. The particles size of these precipitates influence dispersion and adsorption of amine molecules. To measure the size distribution of amine precipitaes, dynamic light scattering technique is used.

According to Malvern Instruments Ltd., dynamic light scattering (DLS) is a technique used to measure Brownian motion and relates this to the size of the particles. DLS is used to measure the size of particles suspended within a liquid. The larger the particle, the slower the Brownian motion will be. An accurately known temperature is necessary for DLS measurement. This is because the viscosity of a liquid is related to its temperature. The temperature should be stable; otherwise non-random movements due to the presence of convection currents in the sample can affect the correct interpretation of particles size. The velocity of the Brownian motion is defined by the translational diffusion coefficient, D.

The size of a particle represented by the hydrodynamic diameter is calculated from translational diffusion using the Stoke Einstein’s equation.

$$d(H) = \frac{kT}{3\pi\mu D}$$

where

D (H) = hydrodynamic diameter

D = translational diffusion coefficient

K = Boltzmann’s constant

T = absolute temperature

μ = viscosity

2.4. Flotation reagents

Flotation is the process of separating mineral particles based on the differences in their surface properties. In potash processing, the mineral components of the ore are not naturally floatable. Separation therefore is impossible without the addition of flotation reagents. The presence of flotation reagents helps to highlight the differences in the surface properties of NaCl and KCl and makes separation possible. These flotation reagents are basically surfactants that perform specific roles during the flotation process to help achieve efficient flotation. Based on their specific functions, flotation reagents may be classified into collectors, frothers, regulators and depressants.

2.5. Collectors used in flotation

Collectors are organic compounds that are added in the pulp or slurry to help separate the mineral of interest from the other components of the ore by making the selected mineral water repellent. Molecules or ions of the collector get adsorbed or adhered onto the surface of the mineral and disrupt the hydrated layers that separate mineral particles from air bubbles so that contact of the bubbles can be made with the minerals enabling the transport of the pulp to the froth phase. The type of collectors which are not soluble in the flotation media usually covers the surface of the mineral particle and renders the mineral water-repellent. Once collector attachment is realised, the mineral components of interest become hydrophobic and can be attached to air bubbles so that recovery of such mineral components can take place. There are various types of collectors used in floatation. Figure 2.5 shows the classification of flotation collectors. The type of collector used in a flotation system is dependent on the type of mineral to be floated. Thus, collectors can be grouped into ionizing collectors and non-ionizing collectors. Ionizing collectors are the group of collectors which dissociate into ions in an aqueous environment.

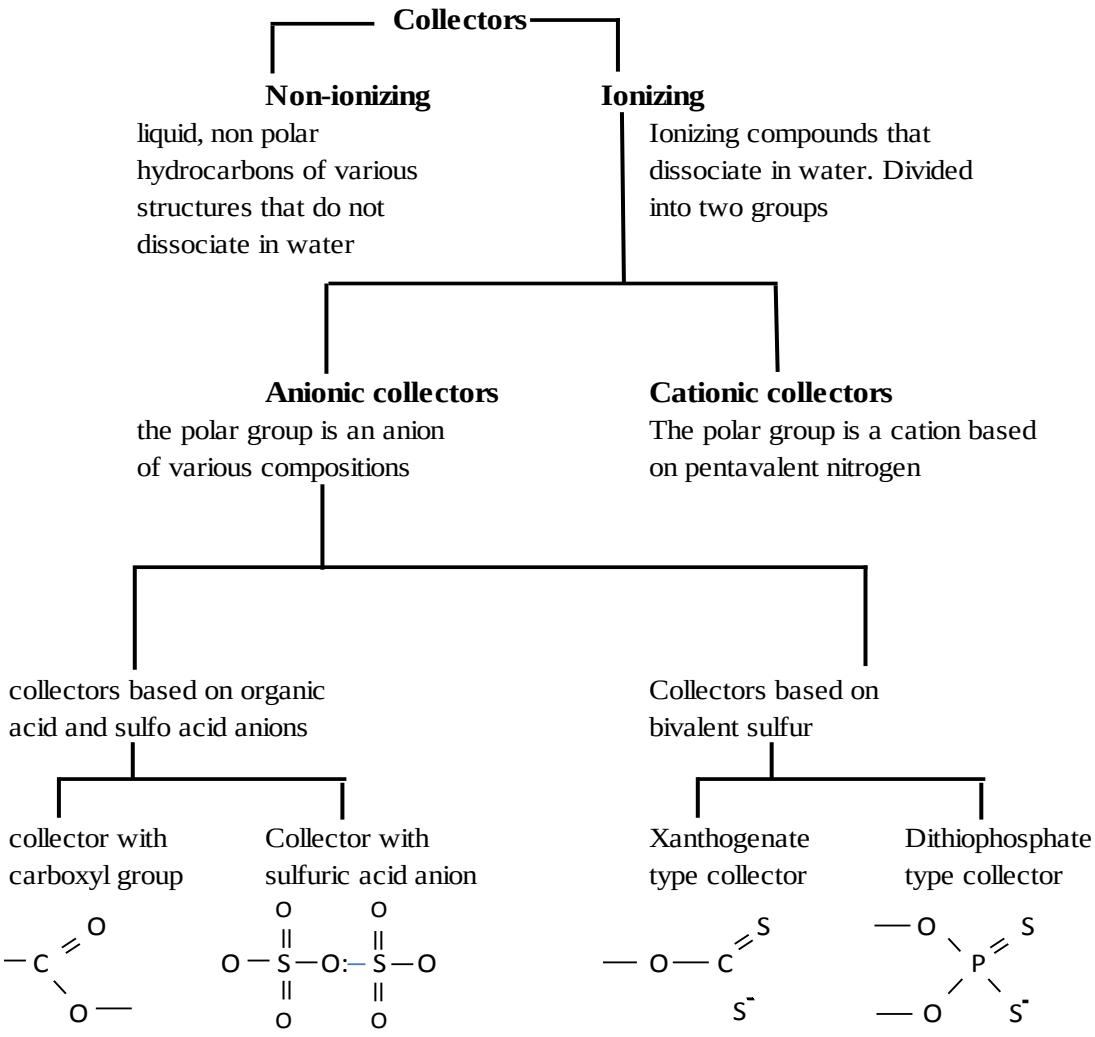


Figure 2. 5. Classification of flotation collectors**.** (Adapted from Wills 2006, Bulatovic 2007).

2.5.1. Anionic collectors

They consist of collectors that are based on organic acid and sulfo acid anions including bivalent sulfur, weak acids or acid salts that ionize in water to produce a collector that has a negatively charged end that will attach to the mineral surfaces, and a hydrocarbon chain that extends out into the bulk solution. Figure 2.6 is a schematic diagram that shows the interaction that occurs between anionic collectors and positive mineral surfaces.

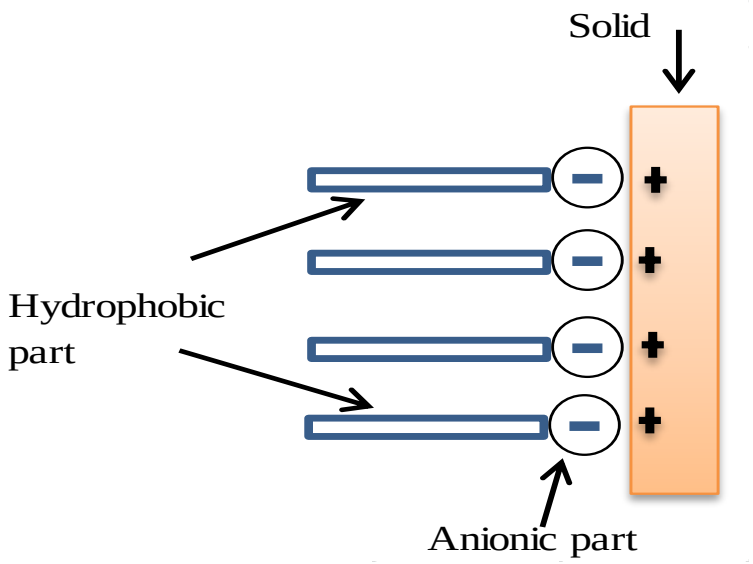


Figure 2. 6 Schematic diagram showing interaction between anionic collectors and positive mineral surfaces.

2.5.2. Cationic collectors

These are collectors which have a cation as their polar group and are based essentially on pentavalent nitrogen. Cationic collectors use a positively-charged amine group to attach to mineral surfaces. Since the amine group has a positive charge, it can attach to negatively-charged mineral surfaces. Figure 2.7 shows the interaction between cationic and negative mineral surfaces. Cationic collectors therefore can attach only to negatively-charged surfaces to bring about flotation.

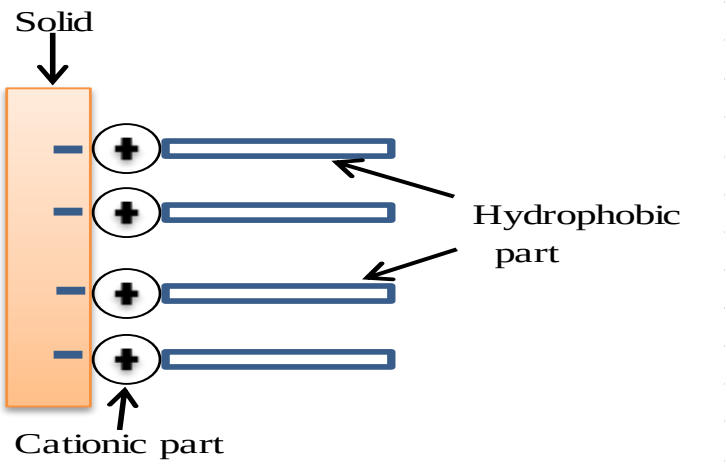


Figure 2. 7 Schematic diagram showing the interaction between cationic collectors and negative mineral surfaces.

They are mainly used for flotation of silicates and certain rare-metal oxides, and for separation of potassium chloride (sylvite) from sodium chloride (halite) in potash processing. There are three types of cationic amine collectors as illustrated in Figure 2.8 and Table 2.2.

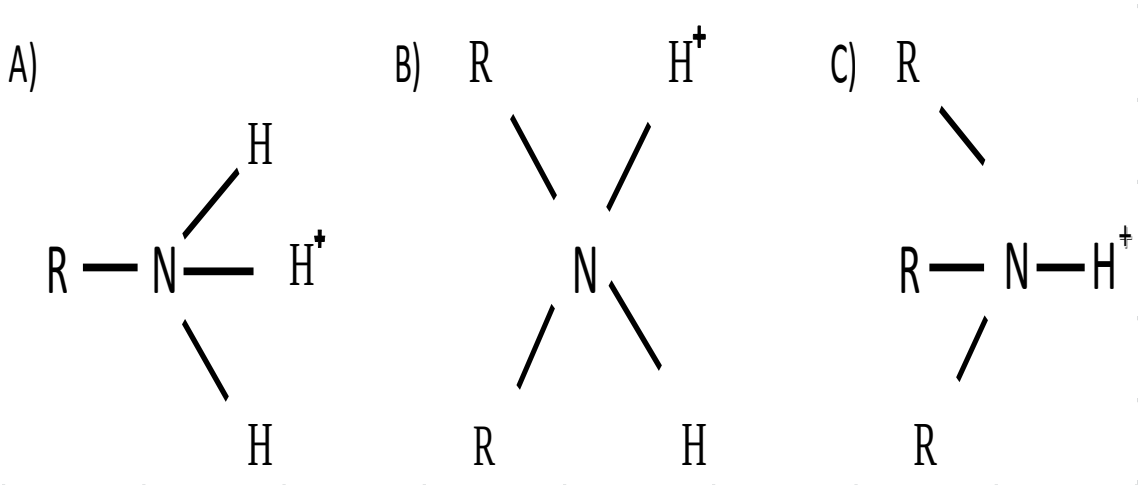
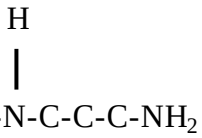
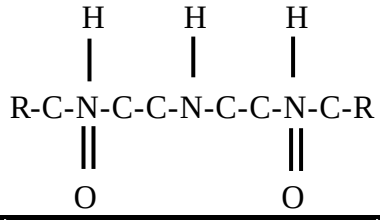


Figure 2. 8 Cationic amine collectors a) Primary amine b) Secondary amine C) Tertiary amine (Adapted from Kawatra, 2001).

Specifically, the cationic collectors that are used in potash flotation are primary long chain amines (RNH_2). They are divided into five main groups: Fatty amines, fatty diamines, ether amines, ether diamines and condensates (Table 2.2). Each of these can be used for different conditions of flotation. For instance, ether diamine has a higher efficiency in winter than fatty diamine but when temperature rises above 25^{o}C in the summer, fatty amines become more efficient (Lin, 1989). The most common cationic collectors used in potash flotation are fatty amines. They are long chain primary alkyl amines with 12-20 carbon chains. Cationic collectors are insoluble in water; therefore they are prepared and used in the form of dispersions. In order to produce stable amine dispersions, an emulsifier in the form of an amine salt is used in amine-in-water-system. Acids such as hydrochloric acid or acetic acids are normally added to amine collectors to form amine salts that become soluble and can form stable emulsions as illustrated in equation (2.4). Most amines foam in the presence of air, therefore care should be taken not to introduce air during the preparation of the collector.

$$RNH_2+HCl = RNH_3Cl + H_20 = RNH_3^{+}{}_{(aq.)} + Cl^{-}{}_{(aq)} \quad (2.4)$$

Table 2.2. Cationic Collectors (Adapted from Bulatovic, 2007; Gefvert, 1986).

Group	Structure	Carbons on Akyle group	Form
Fatty amine	$R\text{-}NH_2$	C_{12}-C_{24}	Solid/paste
Fatty diamine		C_{12}-C_{24}	Solid/paste
Ether amine	$R\text{-}O\text{-}C\text{-}C\text{-}CNH_2$	C_6-C_{13}	Liquid
Ether diamine	$R\text{-}O\text{-}C\text{-}C\text{-}C\text{-}N\text{-}C\text{-}C\text{-}C\text{-}NH_2$	C_8-C_{13}	Liquid
Condensates		C_{18}	Solid/Paste

2.6. Frothers used in potash floatation

Frothers are added to the flotation medium to reduce surface tension and to help stabilize the froth. Thus, in the presence of frothers some compressive forces are generated around air bubbles which prevent the bubbles from bursting. Frothers are heteropolar surface active compounds with hydroxyl (OH), carboxyl (COOH), carbonyl (C=O), and sulpho (OSO_2 and SO_2OH) polar groups and a hydrocarbon radical. Alcohols are the most widely used frothers**.**

2.6.1. Classification of frothers

Depending on their behavior in solution, frothers may be grouped into acidic, basic or neutral frothers. Table 2.3 shows the classification of frothers used in flotation. The performance of a frother according to this classification is based on the pH of the solution in which they are used**.**

Neutral frothers have a wide application in the flotation of most minerals. They represent the most important group of frothers because they can function in acidic and basic media at the same time. The two neutral frothers widely used in potash flotation are methyl isobutyl carbinol (MIBC) from the aliphatic alcohol sub-group and polyglycol ethers (Perucca, 2000).

Aliphatic alcohols are made up of mixtures of different alcohols with different carbon chains as well as mixtures of alcohols and hydrocarbon oils; mixture of C_6-C_9 alcohols, mixture of C_4-C_7 alcohols + hydrocarbon oil and mixture of C_5-C_8 carbon alcohols.

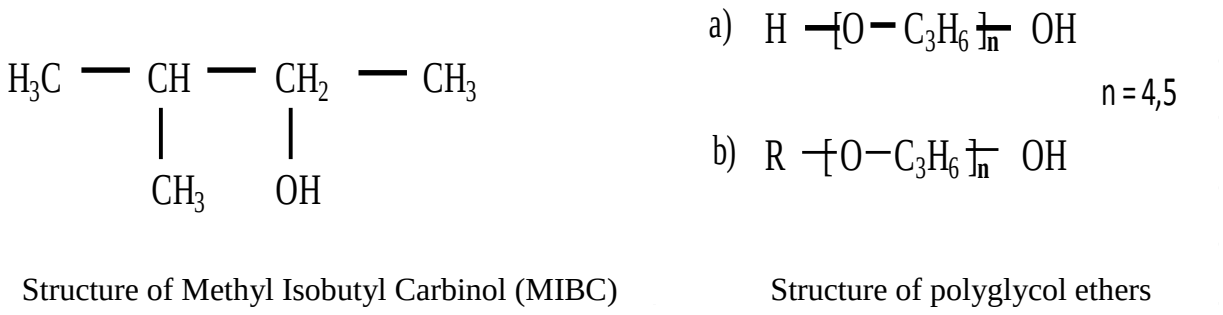
Table 2.3. Classification of frothers (Bulatovic, 2007).

Acidic	**Neutral**	**Basic**
Phenols	Aliphatic alcohols	Pyridine base
Alkyl Sulfates	Alkoxy paraffins	
	Polypropylene glycol ethers	
	Polyglycol ethers	
	Polyglycol glycerol ethers	

Glycol ethers are made from synthetic brake fluid but there are several types of polyglycol ethers produced by different methods depending on the manufacturer. Some polyglycol ethers are produced by condensation with butanol or ethylene oxide or produced as a reaction produced from butanol and caustic soda. The effectiveness and performance of a polyglycol ether frother depends on its carbon length and molecular weight. Bulatovic (2007) stated that the polyglycol ethers from different manufacturers don't behave the same way. He stated that the D13, D14 and D16 polyglycol ethers produced by Hoechst (Germany) were more selective than those produced by Dow, though they had the same structure. He reported that polyglycol ethers produced from butanol and ethylene oxide are more selective and have a better carrying power than the ones produced butanol and caustic soda.

Perucca (2000) also reported that the wide use of MIBC in potash flotation has been due to its ability to deliver fast kinetics, brittle froth and lower water retention which gives high selectivity. He explained however that polyglycol ether has replaced MIBC in recent times in Canada because polyglycol ethers have proved to be more powerful frothers that are able to maintain the

tenacity of frothing and improved recovery of coarse KCl particles. More-over the use of MIBC poses health problems. The structures of MIBC and PGE are shown in Figure 2.9.



Structure of Methyl Isobutyl Carbinol (MIBC) Structure of polyglycol ethers

Figure 2. 9. Structure of common frothers used in potash flotation.

2.7. Regulators

Depressants are one group of modifying reagents that are used in froth flotation. The other group of modifying reagents is called activators. Modifying reagents may also be referred to as regulators because they control the interaction of collectors between components of a mineral or between individual minerals making the collector more selective to certain minerals than others. Thus, regulators function by either increasing the selective adsorption of collector molecules on certain minerals or decreasing the action of the collector on another mineral. If the function of the regulator is to blind the surface of certain minerals to prevent collector adsorption on such minerals, the regulator is said to be a depressant. Activators are used to help condition the surface of certain minerals to promote collector adsorption or adherence on such minerals. The third group of regulators is known as pH modifiers. For the purpose of this research only depressants have been discussed.

2.7.1 Depressant

The role of depressants in mineral flotation is to prevent the flotation of certain unwanted minerals or certain components of a mineral. They are added during the conditioning stage of the flotation process to adsorb, adhere or to cover the surface of gangue (unwanted) minerals thus forming a layer that prevents the surface of the gangue from contacting with collector molecules. Thus, depressants ensure that gangue minerals become hydrophilic (water-loving) and stay in the slurry without floating with the mineral of interest. Unlike slimes coating, a naturally occurring

form of depression, where the slimes can coat every minerals surfaces and impede collector adsorption, (Wills, 2006; Parsonage, 1985) depressants are generally selective towards some selected mineral components usually the gangue minerals. The type of depressants used in a flotation system depends on the mineralogy of the ore being treated. Organic depressants are used in flotation of sulfide as well as non-sulfide minerals. They are grouped into two types; organic polymers and organic acids. Organic polymers which are complex in structure can be modified to have cationic or non-ionic properties. Examples include; starches, ethylene diamine, carboxymethyl cellulose, guar gums etc. Organic acids are used mainly for depression in flotation of oxide minerals. In the flotation of niobium, oxalic acid has been used to depress silica and dolomite. Citric acid and tartaric acid have been used to depress gangue minerals during the flotation of rare earth minerals such as bastnaesite (Bulatovic 2007).

Inorganic depressants are mainly acids, alkalis and salts. Apart from functioning as depressants, the acid and alkali modifiers can also function as pH modifiers and as dispersants. Some acids and alkalis that function as depressants in the flotation process are sulfuric acid, hydrochloric acid, sulfurous acid, lime etc. Examples of depressants are copper sulfate, zinc sulfate, ferro sulfate, ferric chloride etc.

In the flotation of potash, the organic modifying agents are mostly used. Starches, guar gum and derivatives of cellulose have been used effectively as depressants. Starches are prepared from natural sources such as grains of corn, wheat, rice, millet and from potatoes, cassava etc. and treated with an acid or alkali. Carboxymethyl cellulose is the most widely used anionic polymer in mineral flotation. It is prepared by reacting cellulose with sodium acetyl chloride where hydrogen from the hydroxyl group (branched chain) gets replaced by the sodium acetyl group. Sodium carboxyl cellulose forms as a result and replaces a portion of the hydrogen atoms of the hydroxyl groups of the glucose unit and form a cellulose molecule at the end. (Bulatovic, 2007). The structure of sodium carboxymethyl cellulose is shown in Figure 2.10.

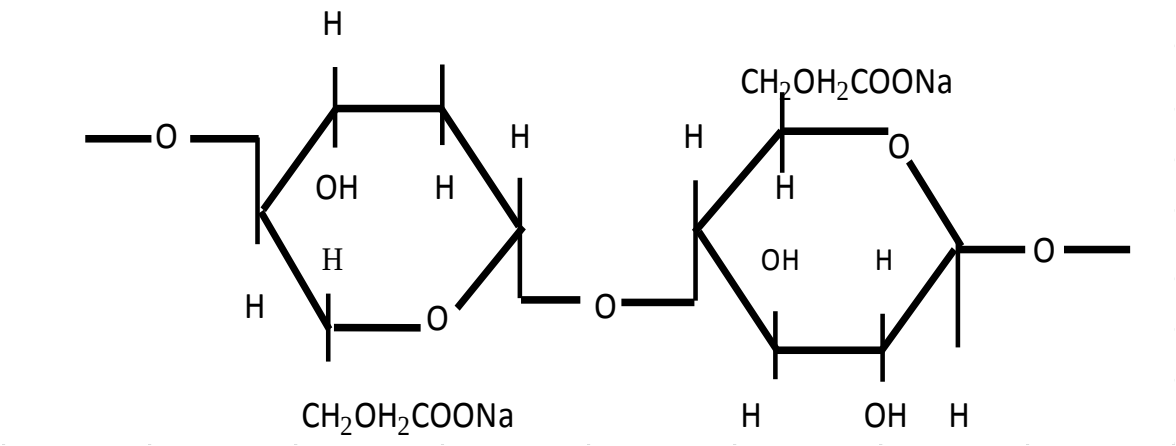


Figure 2. 10. Structure of sodium carboxymethyl cellulose.

2.7.2. Synthetic modifying agents

Polymers of this type are mostly based on polyacrylamides. They are prepared by one of two processes; polymerzation or hydrolysis of acrylamide and by copolymerization of acrylamide with acrylic acid. Figure 2.11 shows the structure of polyacrylamide which comprises acrylamide subunits.

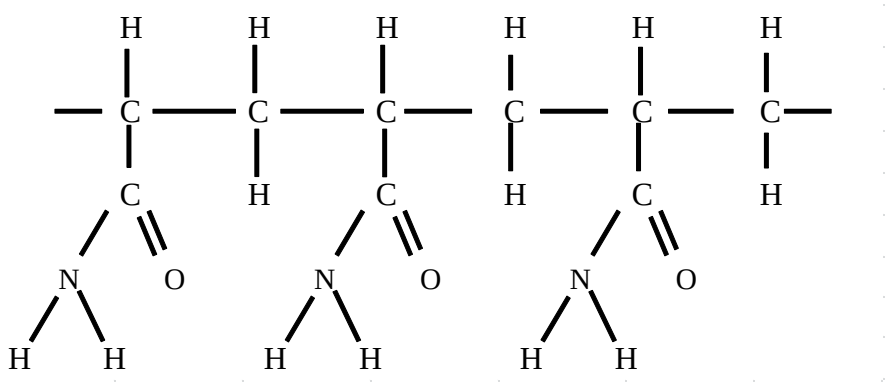


Figure 2. 11. Structure of polycrylamide.

Guar gum has been used as a depressant in mineral processing for a long time. It has a wide application as a flocculant in mineral processing. It is one of the many species of galactomannans. Galactomannans are branched polysaccharides that consist essentially of D-galactose and D-mannose which are found in the endosperm of leguminosae. Guar is therefore

obtained from the seed of cyamopsis tetragonolobus, a legume that grows in India and Pakistan (Goldstein et al., 1973). The structure of galactomannans is shown in Figure 2.12.

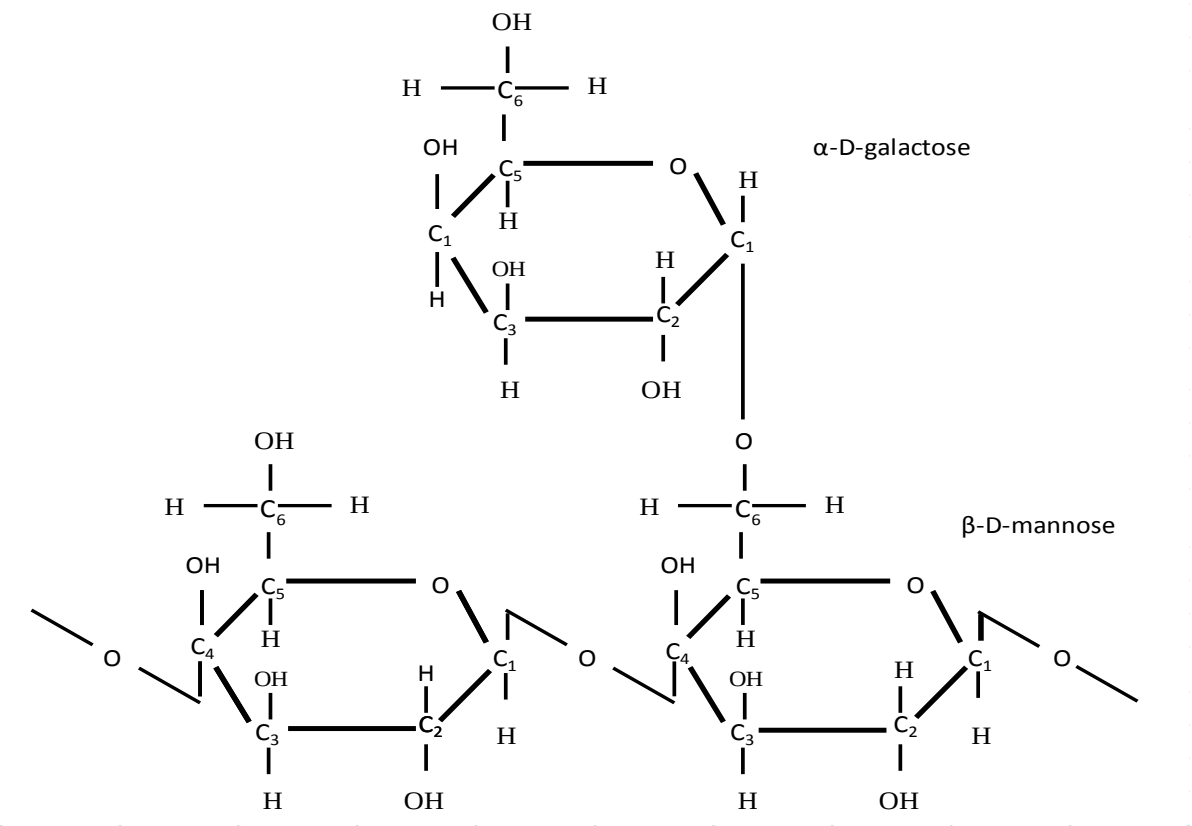


Figure 2. 12. Structure of galactomannan (Perucca, 2000).

2.8. Collector selection for potash flotation

The choice of collector is very important for an efficient flotation process. Many factors influence the kind of collector to be selected but the most important factors include; mineral particle size and temperature. Fine potash particles of sizes from180 µm to 1mm can be floated with most amine collectors of different aliphatic groups. For effective flotation, potash minerals with coarse particle sizes above 1mm must be floated with extender oil in addition to the regular flotation reagents. Depending on the temperature conditions, an amine collector may have to be saturated or an unsaturated aliphatic compound. At high temperatures unsaturated amines with low molecular weight become unstable and ineffective. Amines with high molecular weight and long or branched carbon chains are required for efficient flotation at high temperatures but not at low temperatures (Perucca, 2000).

2.9. Effect of frothers on collector properties

Generally, frothers are the last of the flotation reagents that are added to the flotation system. They are not used during the conditioning stage of the process. Meanwhile, almost all frother types that are used in flotation are alcohols. Alcohols have been found to help increase the spreading rate of amine collectors (Laskowski, 2013, McKercher, 1983). "Leja (1983) claims that the rate of spreading of amine films which are very low in saturated brine, increases dramatically in the presence of alcohols" (Wills, 2006). Burdukova et al, (2009) used methyl isobutyl carbinol (MIBC) which is an alcohol, in combination with dodecylamine and found that in the presence of MIBC, the spreading rate of amines is significantly improved. Thus, MIBC acts as a strong dispersing agent affecting both the size and morphology of amine particles in solution.

2.10. Soluble salt flotation

Soluble salt minerals include sylvite, halite, potassium nitrate, sodium nitrate, phosphates, and sodium bicarbonate including double salts such as carnallite, kainite and schoenite. Sylvite and halites, the major components of sylvinite, are soluble in water. For this reason the medium for separation has to be a saturated solution to prevent the minerals from dissolving. In essence, the component of interest is not supposed to dissolve in solution and therefore saturated brines are used. The saturated brines are highly concentrated electrolytes with high ionic strength which results in an electrical double layer. When introduced in solution, a compressed electrical double layer is formed and this acts to reduce the range of the electrical forces operating between the particles of the medium.

At the same time, surfactants used in soluble salt flotation are mostly insoluble in the saturated brine (Laskowski, 2013). Unlike soluble collectors that are mainly used in the flotation of oxide and sulfide ores, collectors used for floating soluble minerals like potash and phosphate are insoluble and cannot diffuse through the medium and render the mineral of interest floatable. The surfactant molecules rather spread at the air-liquid interface when they get in contact with the rising air bubble (Perruca, 2000). On making contact with air bubbles, surfactant molecules form a compressed monolayer on a definite area per molecule at the surface of the air bubble. Surfactant molecules may also form a hydrophobic layer on mineral particles. It therefore

happens that some bubbles may be attached with surfactant molecules in which case such bubbles may be loosely referred to as ‘activated bubbles’ (Laskowski, 2013). Surfactant molecules may also adhere to mineral particles according to the surface charge model and may also be referred to as ‘activated minerals’. The pulp or the flotation media is stirred up by the agitator to increase the probability of particle-bubble attachment. Particle-bubble attachment may occur if a high degree of adhesion is developed on contact; when a hydrophilic mineral (‘none activated) comes into contact with an ‘activated bubble’ (air bubble which is covered with a spread surfactant) then attachment occurs. Attachment also occurs when a mineral that is covered by hydrophobic layer formed by surfactant molecules (activated mineral), comes into contact with ‘unactivated bubble’.

2.11. pH Control

Most of the modifiers used in froth flotation are pH controllers. They are either acidic or alkaline in nature, while others are neutral. It is interesting to note that pH plays a very important role in flotation as selectivity or floatability of certain components of a mineral ore depends on the pH of the separation medium. Mostly, flotation is carried out in alkaline or near neutral pH because most collectors are stable at alkaline to neutral ph. Another reason is that piping, flotation cells and reagent storage tanks are susceptible to corrosion under acidic conditions. Also, the surface chemistry of most minerals is affected by pH. For instance, some minerals can develop a positive surface charge under acidic conditions and a negative charge under alkaline conditions (Perucca, 2002). For example, in the flotation of potash with amine collectors, the general practice is to float KCl and this takes place at a pH around 6.5. However when the pH of the saturated brine is above 10, NaCl begins to float together with KCl (Schubert, 1967). This is because surfaces of minerals change from being negatively charged to being positively charged at a certain pH interrupting the attraction between the collector and the mineral. The pH of pulps or slurry can therefore be controlled by chemicals such as lime, sodium carbonate, sodium hydroxide, ammonia etc. Sulfuric acid, sulfurous acid etc. are also used where a decrease in pH is required (Wills, 2006).

2.12. Theories of froth flotation

A number of theories have been proposed to explain how flotation of potash takes place. Among these theories are; 1) Ion exchange model (Gaudin, 1957), 2) Heat of solution model (Rogers and Schulman, 1957), 3) Surface hydration model (Schubert, 1967), 4) Surface charge model (Roman et al., 1968; Yalamanchili et al., 1993), 5) Interfacial water model (Hancer et al., 2001) and 5) Law of matching water affinity.

2.13. Ion exchange model

This theory suggests that KCl can be floated with amines because the RNH_3^+ collector ions can fit into the K^+ surface sites of the KCl lattice, which is not the case for NaCl as further explained by the Fuerstenaus in 1956. They mentioned that amine collectors can float only those minerals with cation size similar to that of RNH_3^+. Meanwhile, Roman et al. (1968) reported that there are several exceptions to this rule and that certain sodium minerals actually float as well, even though the collector ions and the surface charge of such salts do not match.

2.14. Heat of solution model

According to this model adsorption of collectors take place by ion hydration instead of crystal geometric conditions. The theory demonstrates that weakly hydrated minerals can be floated with alkyl amines and alkyl sulfates while strongly hydrated minerals can be floated with fatty acids. Very strongly hydrated minerals however cannot be floated at all. (Perucca, 2003).

2.15. Surface hydration model

In this model Schubert, 1967 observed that the adsorption of n-alkyl ammonium cations on sylvite increases suddenly when the concentration of amine in the brine approaches its solubility limit. This showed that the degree of crystallization of the amine is relative to the degree of adsorption. It was found that in the flotation of sylvite the solubility limit of the collector in the brine must be exceeded in order for flotation to take place. This was confirmed by Roman et al. (1968) when they reported that adsorption of amine on KCl did not occur until precipitation of the amine had occurred in solution. They verified this by using dodecylamine and tetradecylamine in an experiment and noted that KCl is floated well only after precipitation has occurred. “The configuration of the collector salt RNH_3Cl (aq.) suggests asymmetry of electrical

charge because of the lack of asymmetry of the molecule. Further, it seemed likely that the negative end of the amine chloride dipole is directed toward the chloride end. These correlations suggested to Roman et al that an electrical mechanism may be involved" Carlos Francisco Perucca (2002). Laskowski et al. (1989) were able to show by studying electrophoretic mobility that dodecylamine precipitate is positively charged up to pH of 11. Miller et al. (1994) were also able to use electrophoretic mobility to determine that the surface charge of KCl and NaCl were negative (-0.47 ± 0.26 μm/sVcm) and positive + 0.171 ± 0.14 μm/(sVcm) respectively. This development gave rise to a theory known as the surface charge model.

2.16. Surface Charge Model

According to the surface charge model, the governing mechanism for soluble salt flotation is electrostatic interaction between the salt surface and collector species (Roman et al., 1968). Roman et al. (1968) reported that KCl and NaCl are opposite in surface charge, KCl being negatively charged and NaCl being positively charged in their saturated brines. These speculations were later confirmed by non-equilibrium electrophoretic mobility measurements (Miller et al., 1992). This implied that the flotation separation of KCl ahead of NaCl is possible due to the adsorption of positively charged collector colloids at the negatively charged KCl surface but not at the positively charged NaCl mineral surface (Miller et al., 1992; Yalamanchili et al., 1993). Thus, a hydrophobic state is obtained at the KCl surface, and flotation separation from the hydrophilic NaCl is achieved. However, this model could not explain the fact that negatively charged KCl can be floated with sodium decyl sulphate which is an anionic collector and therefore has the same charge as KCl.

2.17. Interfacial water structure model

The explanation given for the surface charge model failed to explain the fact that KCl with a negative surface charge can be floated equally well with sodium dodecyl sulfate (SDS) which is an anionic collector. This was revealed by Rogers and Schulman (1957), Schubert (1988), and Hancer et al. (2001). Thus, in contrast to the surface charge model, Rogers and Schulman had the view that the flotation of soluble salts occurs due to the degree of ion hydration at the surfaces of alkali halide salts. Hancer et al. (2001) did further studies and showed that soluble salts float due to hydration phenomena at salt surfaces and attributed the possibility of flotation of alkali salts

(even when the collector has the same charge as the salt surface) to the interfacial water structure model. According to this model, a salt may be water structure maker or a water structure breaker. The structure maker salts interact strongly with water molecules in brine solutions while the structure breaker salts on the other hand have a tendency to break the structure of water at the salt surface; thus they are weakly hydrated.

Adsorption of surfactant in weakly hydrated salts is higher, therefore, hydrophobicity is facilitated which consequently allows flotation of such salts to take place (Du and Miller, 2007; Du et al., 2007; Hancer et al., 2001; Ozdemir et al., 2006). This is why KCl which is water structure breaker can be floated with cationic collectors such as DDA and ODA and with anionic collectors, such as sodium dodecyl sulfate (SDS) irrespective of the charge of the collector and the surface charge of the salts. This theory explains that NaCl, cannot be floated because it is a water structure maker and rather stabilizes the interfacial water structure at the salt/brine interface. From Figure 2.13 it can be seen that adsorption of amine molecules on KCl is easier than adsorption on NaCl because of stronger interactive action that exists between water molecules and the strongly hydrated NaCl.

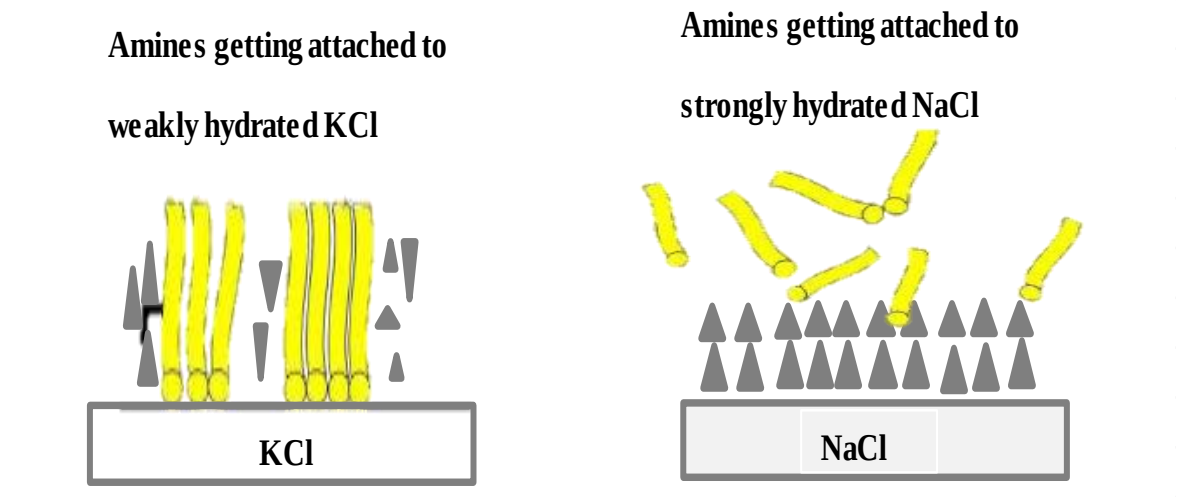


Figure 2. 13. Adsorption of amine molecules on KCl and NaCl. The KCl is weakly hydrated whiles the NaCl is strongly hydrated. (Ozdemir et al, 2011).

2.18. Law of matching water affinity

According to this theory halide ions may either be kosmotropic or chaotropic. Kosmotropes are halide ions such as Li^+, Na^+ and F^-; that are strongly hydrated in solution whereas chaotropes such as K^+, Rb^+, Cs^+, Cl^-, Br^- and I^- are weakly hydrated in solution. Ozdemir (2011) explained

the theory as proposed by Collins (2004) that when the constituent ions of a salt have matching water affinities (chaotrope-chaotrope or kosmotrope-kosmotrope) then the interaction with water are weak and flotation will occur with such salts. On the other hand, when the water affinities of the constituents of the salt do not match (chaotrope-kosmotrope) then interaction with water is strong and flotation of such salts is not likely to occur. Ozdemir (2011) showed the correlation of the floatability of alkali halide with combinations (Table 2.4). From Table 2.4, Ozdemir explains that LiF is floatable because Li^+ and F^- are both strongly hydrated (kosmotropes) and their combination forms the closest ion pairs which are less hydrated than separate ions. KCl can also be floated because K^+ and Cl^- are both chaotropes. NaCl is not likely to float because the water affinity of its constituent ions; Na^+ and Cl^- are not the same (kosmotrope-chaotrope). This makes interactions with water very strong creating a barrier that impedes flotation. Thus this theory is a step up to the interfacial water structure model.

Table 2.4 Correlation of the floatability of alkali halide (Adapted from Hancer et al, 2001).

	F-	**Cl-**	**Br-**	**I-**
Li+	F	NF	NF	NF
Na+	NF	NF	NF	NF
K+	NF	F	F	F
Rb+	NF	F	F	F
Cs+	NF	F	F	F

Keys: NF = No Flotation, F = Flotation occurs

2.19. Mechanism of potash flotation

So far the most prevalent models that appear to be able to explain the mechanism of flotation in potash processing are the surface charge model and the interfacial water structure model. Alkyl amines and carboxylates have stood out to be the main collectors for potash flotation. In brine solutions these collectors don't dissolve but precipitate to form collector colloids. It has been found by electrophoretic mobility technique that KCl particles have negative charge in saturated

brines. Also, the amine precipitates that form from the addition of amine emulsions with saturated brine, carry a positive charge in solution. Figure 2.14 is the structure of alkyl amine.

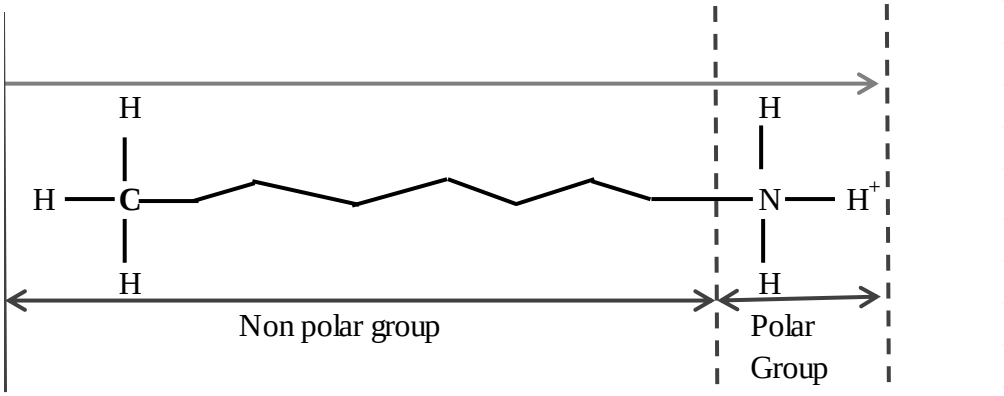


Figure 2. 14. Structure of alkyl amine with the polar group carrying a positive charge.

Polar group of the amine collector has the ability to interact with any potash component with a negative surface charge and cause adsorption or attachment to take place. However the ability of amine colloids/precipitates to get attached to potash particles and cause hydrophobicity is determined by the strength of the cohesive forces existing within the water molecules surrounding the potash particles. As explained in section 2.16, KCl has a negative surface charge while NaCl has a positive surface charge in saturated brine at a pH of 6 to 7. As long as the pH is within this range, amine precipitates will get attached to KCl by virtue of electrostatic attraction that exist and float while NaCl stays in solution. This suggests that three main steps take place to bring about flotation; Selectivity, adsorption and hydrophobicity.

2.19.1 Selectivity

When the amine collector is introduced into the brine, precipitates of amines are formed. These white precipitates or collector colloids are not able to reach the surface of NaCl particles because of the strong interaction of water molecules at its surface acting as a barrier against attachment. The collector colloids are able to reach the surface of KCl because KCl is not strongly hydrated in brine.

2.19.2 Adsorption/amine attachment

As the amines approach the surface of KCl particles they get attached as a result of electrostatic attractions that exist between them. The finer precipitates also get coated on the air bubbles and spread into a molecular film (Laskowski, 2013). The polar side of the amine gets attached on the KCl surface and the non-polar side directed into the bulk of the brine solution in the fashion as presented in Figure 2.15.

2.19.3 Hydrophobicity

The amine precipitates have a polar side (head) and a non-polar side (tail). Adsorption on the KCl particles or the solution-gas interphase is done by the polar side. The tail side, which is non-polar, is directed away from the bulk solution in a fashion as if to get out of solution. By that action, where the polar side of the attached amine precipitate tries to get out of solution, hydrophobicity is imparted to the potash particle and with the help of the air bubbles potash particles are floated to the surface in a stabilized froth and skimmed off. During agitation of the brine solution, active bubbles, the bubbles that are coated with amine collectors are able to pick up KCl particles whereas KCl particles which have adsorbed amine are able to get attached to an "inactive bubble" (bubble that has not been coated with amines). However, Burdukova and Laskowski (2009) have shown that when KCl particles get attached to "active bubbles" they become more hydrophobic as compared to when KCl particles coated by precipitating amines get attached to bubbles (inactive). This implies that for more hydrophobicity, the precipitating amine should be able to quickly spread at the solution-gas interphase into a molecular film. This is possible when other surfactants such as frothers and organic additives are also employed.

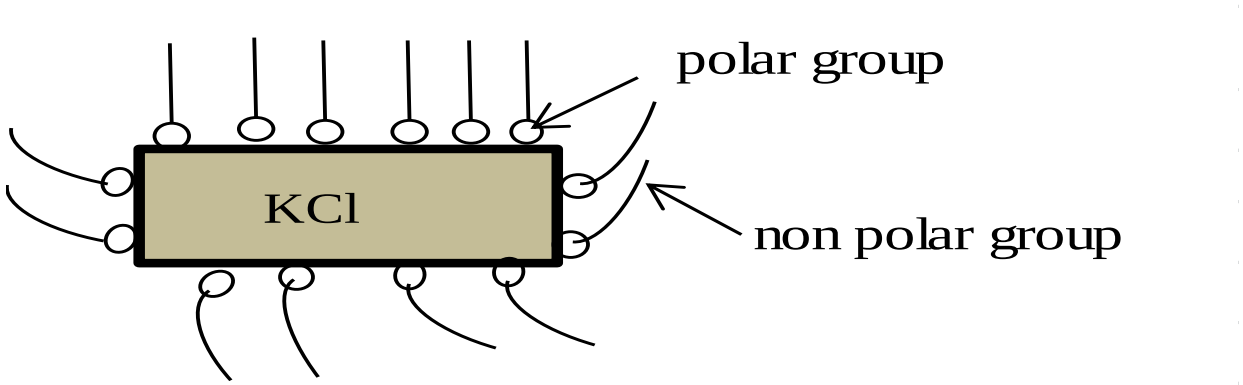


Figure 2. 15. Attachment of amine collectors on KCl surfaces.

The precipitates that form when amine is introduced into brine appear in different sizes and shapes. It appears as if the finer precipitates get attached or coated on air bubbles whereas the medium to coarse precipitates get attached onto KCl particles. The bigger precipitates supposedly do not do any attachment but settle at the bottom of the flotation cell and can be seen as white precipitates after the flotation process.

2.20. Effect of temperature on flotation

Seasonal temperature variations may have adverse effect on the processing of potash ores. Variations in temperature can affect every unit of the processing plant, starting from milling, classification, thickening, filtration and most importantly, flotation (Lin, 1988). When these process units are negatively affected, it leads to a reduction in the recovery of potash. Temperatures may vary from day time to night time and from summer to winter and this must be factored into the initial design of a processing plant. Temperature has effect on the kinetics of flotation. It often results in poorer selectivity. This has been observed particularly for fluorspar and for mixtures of sphalerite and chalcopyrite. Temperature also affects the pH of pulp, the viscosity of the pulp and the formation of bubbles. (O'Connor et al., 1984).

In general temperature variation below or above the design level of a plant may cause serious plant performance issues. However, when the unexpected happens, measures must be put in place to minimize the effect they will have on production. In Saskatchewan, Canada the potash industry is more often faced with low temperature problems due to longer winter seasons. Possible solutions to low temperature issues in flotation include:

Increasing temperatures: This can be achieved by preheating the feed air, the dispersions of the collector aggregates and increasing the speed of the agitator or by increasing the residence time by addition of extra flotation cells or recycling flotation tailings. According to Lin (1988), the above solutions are expensive and the collector should be changed if any of these solutions are not beneficial. However, changing a collector may also involve a lot of time for research and development.

Huang Qimao et al., (2009) developed a new α- amino acid based collector using industrial rapeseed oil as the raw material for low temperature flotation. They did a comparative study of the new collector with the conventional fatty acid collector on phosphate which is also a water

soluble ore and found that α- amino acid based collector improved solubility of the collector, reagent consumption and the floatability of the phosphate.

Wilson et al. (1969) patented the method of obtaining desired mineral values from potash ores by froth flotation at temperatures between 8° C to 20° C In their patent they developed a flotation reagent for low temperature flotation which comprises a mixture of alkyl and alkenyl amine components selected from the group consisting of primary aliphatic amines containing long straight chain hydrocarbon groups of 16 to 18 carbon atoms and their water soluble acid addition salts.

Other researchers looked at the effect of alcohol on collector adsorption and flotation efficiency (Monte and Oliveira, 2004; McKercher, 1983). The general conclusion was that the addition of alcohol increases the rate of amine adsorption and potash flotation and the higher the carbon chain of the alcohol, the higher the flotation efficiency. Monte and Oliveira (2004) however showed that octanol improved flotation efficiency more than butanol and decanol and the higher the concentration of octanol the higher the efficiency of flotation. "Leja (1983) claimed that the rate of spreading of amine films, which is very low in brine, increases dramatically in the presence of alcohol" (Wills, 2006). It therefore follows that alcohols can also be used to improve flotation from low temperature brines looking at the fact that the problem encountered during low temperature flotation (which is poor dispersion of the collector) can be dealt with in the presence of alcohol according to Leja (1983).

Flotation of potash ores like sylvite depends on the formation of insoluble collector species. "Increased temperature enhances solubility of amines", Gefvert, (1987) and therefore impedes flotation. To counter the negative effect posed by increased temperature, long or branched chains are used since they have bigger molecular weight and are not easily soluble. In general, amines with longer chain lengths are used during summer or during the day while amines with shorter chain lengths are used during low temperatures (winter or during night shifts). On the other hand, amines become more insoluble when temperature is low which logically, must improve flotation if it is true according to Gefvert that sylvite flotation depends on formation of insoluble collector species. The effect of temperature also influences the choice of amine collectors with regards to the degree of saturation which is characterized by the iodine value. When temperature goes high, the amine used must have a higher degree of saturation whereas lower temperatures require

higher degree of unsaturation to keep the amine collector effective. Wilson et al., (1969) argued that temperature conditions can vary over a short period of time making it necessary to come up with a collector that can be used effectively over a wide range of temperature without having to alter the degree of amine unsaturation to match up with the temperature. In their patent, (US Patent #3424310), they developed a combination of reagents consisting of an admixture of alkyl and alkenyl amine components and aromatic oil to be able to recover mineral values over a wide range of temperature.

2.21. Effect of Organic additives on flotation

Burdukova and Laskowski (2009) mentioned in their work that improved flotation efficiency is due to dispersion of amine in the brine and the precipitation of amine on the bubble surface (Burdukova and Laskowski, 2009). This is suggestive of the fact that to improve the efficiency of amine its rate of dispersion is crucial and as such any modification has to be focused on improving dispersion. This can be made possible by the addition of certain additives in the flotation process.

2.21.1. Urea

Urea and its derivatives have the ability to change some properties of surfactants in their aqueous solution. El-Aila (2005) explained that the mechanism is such that in an aqueous solution, urea can weaken the water-water interaction that takes place. It does this by replacing several water molecules from an apolar solvation shell (El-Aila, 2005). In effect, instead of a strong hydrogen-hydrogen interaction which is characterized by strong cohesive force, urea interacts with the hydrogen molecules and weakens the cohesion between water molecules. In flotation, a weaker interaction between water molecules enhances surfactant attachment to air bubbles and potash particles which is necessary to enhance efficiency of amine collectors**.** El-Aila, (2005) studied the effect of urea and salt on micelle formation of zwitterionic surfactants and found that the critical micelle concentration of the surfactants is altered in the presence of urea El-Aila, (2005). Viscosity measurements were used to study how the combined presences of a salt and organic additive such as urea influence the viscosity and the overall organization of surfactant molecules El-Aila, (2005). Briganti et al. (1991) studied the effect of urea on micellar properties of aqueous solutions of non-ionic surfactants and found that in the presence of urea; the critical micelle

concentration increases, the size of the micelles decrease and the sphere-to-rod shape transition temperature shifts to higher values Biganti et al, (1991). Several researchers have reported that flotation takes place from the onset of micelle formation. A higher critical micelle concentration means a faster formation of micelles which implies a higher rate of flotation. Smaller sized micelles and rod shaped micelles imply micelles with larger surface area and this is important for particle-surfactant attachment and surfactant-bubble attachment which must take place before flotation can occur.

Some derivatives of urea have been discovered to improve flotation. Perkins and Sayre (1921) stated in their patent that the addition of aromatic thio-urea compounds, such as thiocarbanilid or diphenyl-thiourea to the mineral pulp improved flotation of sulfide ores to a recovery of about 90%. Urea fomaldehyde can help to improve potash recovery and help cut down on reagent consumption. Navarette et al employed the use of urea formaldehyde to condition pulped potash ore for potash flotation with little or no frother and obtained a mineral recovery that is equivalent to that obtained when full dosage of frother was used (without urea formaldehyde resin) (Navarrette et al., 2006).

2.21.2. Oils

Pine oil and corn oil have been used as auxiliary reagents to help improve flotation recovery. They are usually referred to as auxiliary reagents because they cannot be used by themselves alone. They help produce better results when they are added to other reagents. When thiocarbinilid is used with pine oil, excellent results are obtained from the flotation of porphyry ores (Perkins and Sayre, 1921). Pine oil, with some ores may have both frothing and selective qualities (Perkins and Sayre, 1921). In general organic additives act as solvents for flotation reagents. They help increase the dispersion and dissolution of flotation reagents in their aqueous solutions and this is very helpful for low temperature flotation of potash. In Martin Wilson's 1970 patent, it was stated that aromatic oils are especially suitable for low temperature flotation because they have low pour points and also viscosities stay low at low temperatures. He made the assumption that almost any mineral oil, aromatic or aliphatic liquid at a fairly low temperature of operation, should be able to dissolve a fairly high saturated amine at such a low temperature.

2.21.3 Alcohols

Alcohols are the main organic additives that have been used to aid flotation. In the flotation of potash, alcohols have been used as solvents for collector reagents. The selectivity of terpineol, one of the organic alcohols that have found application in flotation is comparatively low but it has a very good frothing abilities. Early research compiled by McKercher (1983) reported that generally, the longer the carbon chain of the alcohol, the faster the spreading rate of the amine aggregates and the higher the potash recovery, Figure 2.16.

However, the work of Monte and Oliveira (2004) showed that alcohol with a longer carbon chain does not necessarily enhance flotation more than an alcohol with a shorter carbon chain. In their work, it was shown that there is an optimum length of alcohol chain for higher flotation efficiency. They performed flotation experiments with butanol, octanol and decanol and found that octanol with a carbon chain of 8 gave a higher flotation efficiency than butanol (4 carbon chains) and decanol (10 carbon chains). It was observed that butanol with a shorter carbon chain gave a very low efficiency, it was not an implication that decanol with the highest carbon chain would give the highest efficiency. Octanol which has 8 carbon chains gave the highest efficiency and it was shown that the efficiency of flotation increases with the concentration of the octanol to some extent. Thus, flotation with octanol gives the highest efficiency. It was shown that the adsorption density of dodecylamine was highest when octanol was added to the dodecylamine dispersion. Factors that contribute to high amine adsorption include high dispersion rate of amine and smaller particle size of the amine aggregates/precipitates. It means that in the presence of octanol, the particle size of dodecyl amine precipitates are reduced and are significantly dispersed in the solution.

Some types of alcohols like octanol and methyl isobutyl carbinol (MIBC) have mostly been used as frothers for potash production. According to Burdukova et al (2009), when MIBC is mixed with amine before addition to the brine it helps to increase dispersion rate and reduce the particle size of the amine precipitates which are positive factors for efficient flotation. Figure 2.17 shows optical images of the DDA particles in a rapidly cooled suspension with (a) MIBC present in the DDA emulsion, (b) MIBC present in the brine, (c) in the absence of MIBC. In the absence of MIBC (Figure 2.17(c)) the amine precipitates become poorly dispersed and form bigger particles

which are not good for flotation. It means that the use of MIBC in potash flotation provides a dual function as amine dispersant and as a frother.

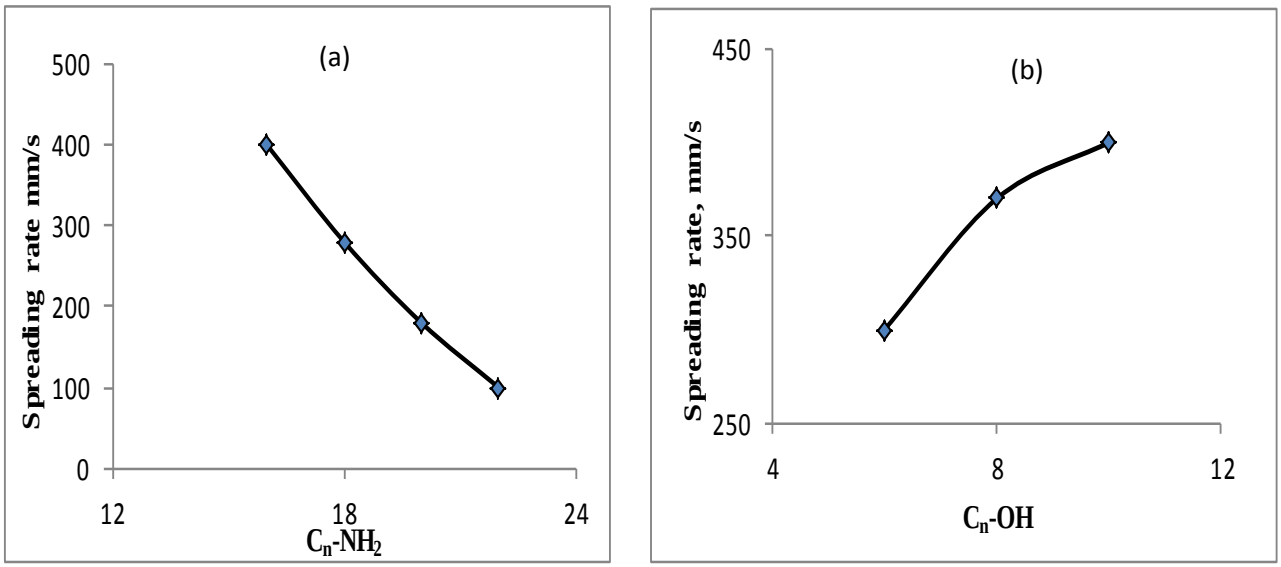


Figure 2. 16. (A) Effect of carbon chain on spreading rate of amine (B) effect of carbon chain of alcohol on spreading/ dispersion rate of the amine. (Reproduced from McKercher et al., 1983).

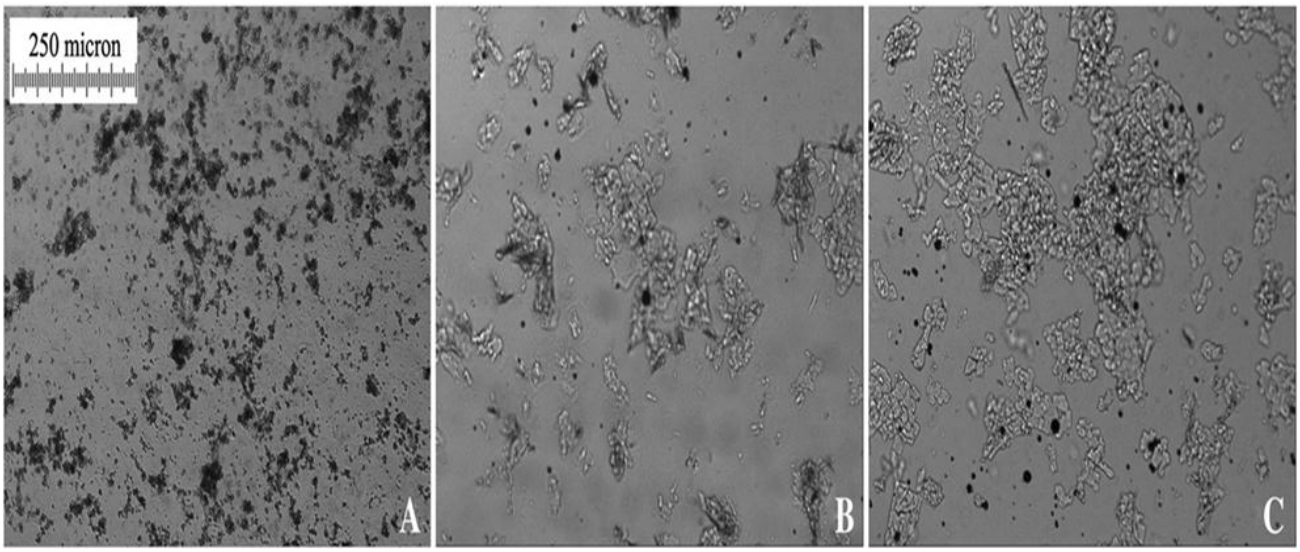


Figure 2. 17. Images of DDA particles in a rapidly cooled suspension (A) with MIBC present in the DDA emulsion, (B) with MIBC present in the brine, (C) in the absence of MIBC (Burdukova et al., 2009).

3. MATERIALS AND EXPERIMENTAL PROCEDURES

3.1. Reagents

All reagents/chemicals were used as received, without further purification. They were purchased from Sigma Aldrich, Ontario, Canada or Alfa Aesar, Ontario, Canada. The reagents used include, Dodecyl amine, (DDA), Hexadecyl amine (HDA), Octadecyl amine (ODA), Methyl Isobutyl carbinol (MIBC), Polyglycol ether (PGE), urea and alkyl alcohols.

3.1.1. Collectors

Dodecylamine (DDA) with a purity of 99.0% was purchased from Sigma Aldrich. Solutions containing 0.5 wt. % DDA were prepared by pouring 0.5 g of DDA into a round bottomed flask and heating at 70^{o}C to melt. 100 ml of HCl acidified deionized water heated at the same temperature (70^{o}C) was added to the content in the round bottomed flask. The flask was fitted with a condenser and the amine dispersion was continuously stirred for 10 minutes using a magnetic stirrer until an emulsion was formed. A condenser was used in order to prevent the loss of some of the reagent through evaporation and also to serve as a cover and prevent interaction with air which could lead to foaming of the amine solution. The other amine collectors were also prepared in like manner.

3.1.2. Frothers

The frother used in this experiment was, Polyglycol ether which was also purchased from Sigma Aldrich, Ontario, Canada. The frother was used as received at a dosage of 50 g/t (reagent concentration)

3.1.3. Depressants

Carboxymethylcellulose (CMC) was used as the depressant and was used at 1% dispersion in water. It was obtained from Alfa Aesar. 10 g of CMC was measured into a beaker and heated at high temperature until it melted. One litre of deionized water was then added and continuously stirred with a magnetic stirrer until all the solids dissolved in solution.

3.2. Additives

3.2.1. Urea

5 wt.% of urea was prepared by dissolving the required 10 g of urea in 200 ml of water at 30^{o}C and stirring continuously with a magnetic stirrer. To prevent precipitation, a condenser was fitted on the beaker containing the urea solution to prevent entry of air and loss of solution through evaporation.

3.2.2. Alcohols

2 v/v% solutions each of polyglycol ether, hexanol octanol, decanol and docosanol were prepared by mixing 2 ml of each alcohol with 100 ml of water and stirred continuously for 10 minutes. During the preparation of docosanol, it was found that it quickly solidifies in the presence of air. It was therefore discarded as it was not going to be useful as an additive though it had the property of reducing viscosity of liquids even at their pour points**.**

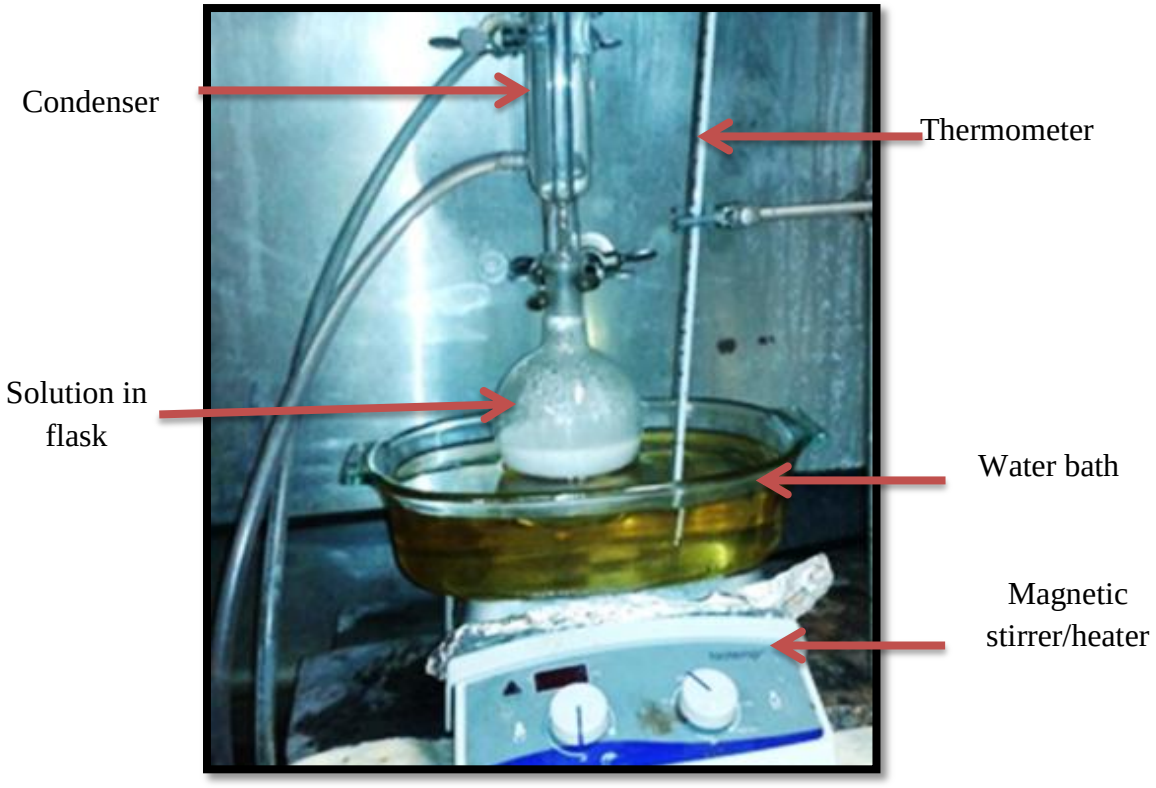


Figure 3. 1. Set up for preparation of reagents.

3.3. Potash ore sample preparation

The potash ore used for this experiment was sylvinite (See Figure 3.2). It was obtained from Mosaic Company, Canada on September 2013.

To make it amenable for flotation, a Torrey Hills ND2L planetary ball mill with stainless steel cups of 285 ml capacity (Figure 3.3) located in room 0C 19 of the Engineering building was used to mill the potash and the mill speed was set at 200 RPM. For an average sylvinite particle size of 4mm, it took 10-15 minutes to mill the ore to sizes below 2mm. Tyler sieves (Figure 3.4) were then used to screen the milled product into different size ranges**.** To obtain particle sizes below 1 mm, five different sieves were used to screen the milled potash. 1.18 µm, 850 µm, 355 µm, 250 µm and 180 µm sieve meshes were used to achieve this. The sieve was arranged in ascending order of mesh size. In the size analysis, {-1.18, +850 µm} means size of particles which passed through 1.18 µm sieve but stayed on the 850 µm size sieve. All +1.18 µm particles were milled again while -180 µm and +850 µm particles were kept and used for brine preparation. A representative sample of the milled ore was analyzed with a PANalytical Empyrean powder X-ray diffractometry (XRD) using a Cu source to determine the initial compositions of KCl, NaCl and impurities. The XRD was set at a scan speed of 0.0265 degrees/second, a step size of 0.0167 degrees, a tube voltage of 45kV and a tube current of 40 mA. The scan range was 10 degrees to 80 degrees 2-theta.

Figure 3. 2. Optical image of sylvinite (potash ore).

Figure 3. 3. Torrey Hills- ND2L Ball milling equipment.

Figure 3. 4. Tyler sieves.

3.4. Dispersion test

The performance of various amines for low temperature flotation was evaluated by dispersion tests. An efficient flotation is possible if the amine precipitates are well dispersed in the brine solution to enhance particle-amine attachment and attachment of film of amine colloids on air bubble. Amine is not soluble in saturated brine. This causes a majority of the amine particles to spread on the surface of the air bubbles making the size of the amine particles a very important parameter. The smaller the size of the amine precipitates, the easier they spread or adhere to the air-liquid interface for KCl flotation to take place. Various dispersion tests were carried out to select candidate amine collector(s) and additive(s) needed for effective flotation at low temperature.

3.4.1. Amine dispersion in saturated brine solution

A drop of DDA-HCl was mixed with hexanol in the mass ratio of 1:2 and placed into a rectangular shaped container measuring 30 cm × 13 cm × 8 cm filled halfway with saturated brine. Hexanol was mixed with amine because long chain alkyl amines have very low spreading tendencies (O'Brien et al., 1983). The amine was dropped into the brine from one end and allowed to spread steadily through the brine until it reached the other end of the container. The time it took for the amine to diffuse from one end of the container to the other end was recorded. This experiment was done inside the fume hood with the air flow turned off to prevent interference with external forces like air that can affect the spreading rate of the amines. The temperatures of the saturated brine used for the dispersion test were in two ranges. In one case, the temperature was 12^{o}C at the onset of the test and at the end of the test temperature increased by 1^{o}C or 2^{o}C. In the second case, the starting temperature of the brine was 30^{o}C and it decreased by about 2^{o}C when the experiment was over. This experiment was repeated using hexadecyl amine hydrochloride (HDA-HCl) and octadecyl amine hydrochloride (ODA-HCl), so that the one with the highest spreading rate in low temperature saturated brine could be selected**.**

3.5. Effect of temperature on amine dispersions

The selected amine collector from the previous experiment (section 3.4.1), DDA-HCl, was used to study the effect of temperature on amine dispersion in brine solution. 10 ml of 2 wt.% DDA-HCl was pipetted into 100 ml of brine solution.

Precipitates of amine were formed after the slurry was stirred. The degree of dispersion and the distribution of amine particles were studied in brines maintained at room and sub room temperatures using a Nikon Optiphot™ optical microscope (Figure 3.5).

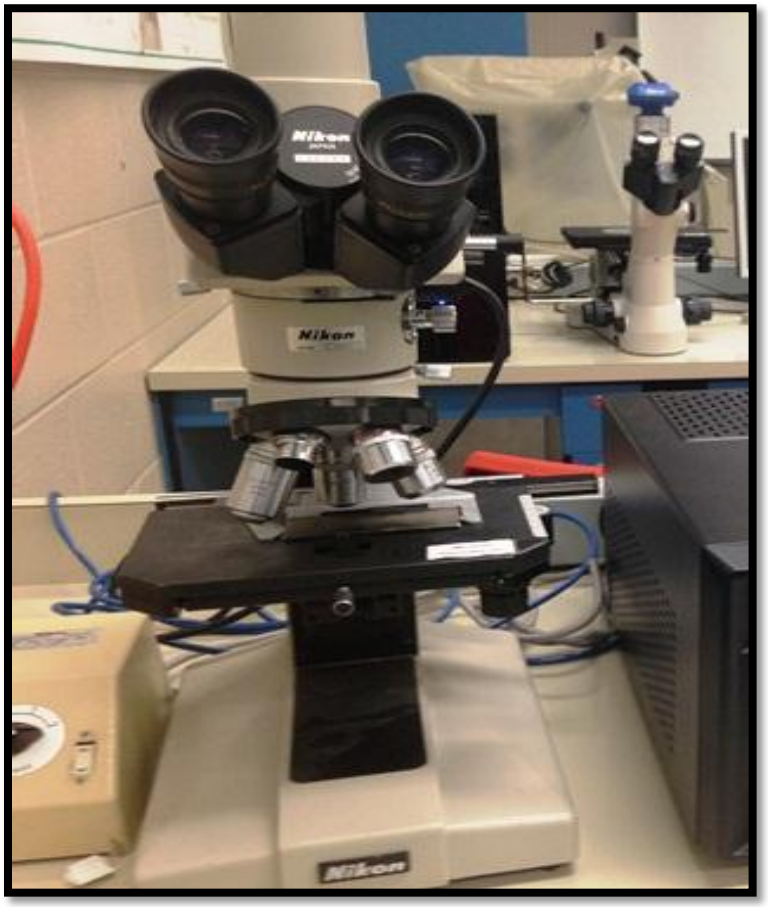


Figure 3. 5. Nikon Optiphot™ optical microscope.

To graphically show the results from section 3.5, dynamic light scattering experiments were also done on specimens to find the size and size distribution of the amine precipitates in low temperature saturated brine (15^{o}C) and saturated brine at room temperature. A Malvern Mastersizer S Long Bench Particle Size Analyzer, Malvern Instruments Ltd., U.K. located in the Engineering building was used for the dynamic light scattering experiment. The size of the lens used was 300 mm (for analyzing size range of 0.5 - 880 μm). 100 ml of saturated salt solution was poured into the sample feeder placed in the path of the laser. 10 mls of 2 wt.% DDA-HCl solution was added and after the obscuration has stabilized, the analysis started. The sample feeder was rinsed five times with deionized water after each experiment to prevent any

interference with the results. After the experiment, the sample feeder was again rinsed several times with deionized water to prevent corrosion of the instrument.

3.6. Effect of alcohol on particle size of amine precipitates

10 ml of 2 wt. % DDA-HCl was prepared using the same process as in section 3.1.1. 2 %v/v each of the alcohols; MIBC, polyglycol ether, octanol and decanol were also prepared. MIBC was mixed with the hot, freshly prepared DDA-HCl in the ratio of 1:1 and stirred with a magnetic stirrer for 5 minutes. 10 ml of the resulting solution was then pipetted into 100 ml saturated brine in a bottle and shaken for 2 minutes. The experiment was repeated for the other frothers. A closer look through the transparent bottles showed that precipitates were formed as expected. Samples of the resulting mixture of amine-frother-saturated brine were taken and dynamic light scattering technique was used to determine the size and size distribution of the amine precipitates that form from the different frothers used.

3.7. Effect of MIBC and PGE on amine dispersion

The purpose of this experiment was to select the best frother for viscosity and flotation experiments. Polished KCl plates used for this experiment were obtained from International Crystal Laboratories. The alcohols that significantly reduced the size of amine precipitates in the previous experiment (MIBC and PGE) were selected and used to prepare a reagent made up of a mixture of amine and alcohol.

MIBC is known to be a very strong collector but due to health issues most potash companies in Canada have stopped using it. However, for the purpose of comparison with the work of Burkova and Laskowski (2009), MIBC was used for further experiments. Three different types of amine emulsions were prepared for scanning electron microscope imaging. DDA-HCl emulsion was prepared according to the procedure in section 3.1.1 in three cases. In case 1, 10 ml of 2 v/v% of MIBC was mixed with 10 ml of 2 wt.% DDA-HCl and then added on 100 ml of saturated brine. In case 2, 10 ml of 2 v/v% PGE was mixed with 10 ml of 2 wt.% DDA-HCl and added to 100 ml of saturated brine. In the third case, 10 ml of DDA-HCl was added to 100 ml of saturated brine without adding any additive. The mixtures in each case were gently stirred to allow for the formation of amine precipitates. Drops of solution from each case were deposited on polished KCl plates measuring 12.5 mm×12.5 mm× 12.5 mm and allowed to spread on the

smooth surface. They were left in the fume hood for 16hrs to allow the water component in it to dry out. The amine particles on the polished KCl were then examined using a Hitachi SU6600 scanning electron microscope (SEM) located in 3C 95 in the Engineering building and images were taken. At 10 kV, it was difficult to visualize the amine particles because the KCl was charging. The voltage was then reduced to 5 kV before images could be taken. The SEM is shown in Figure 3.6.

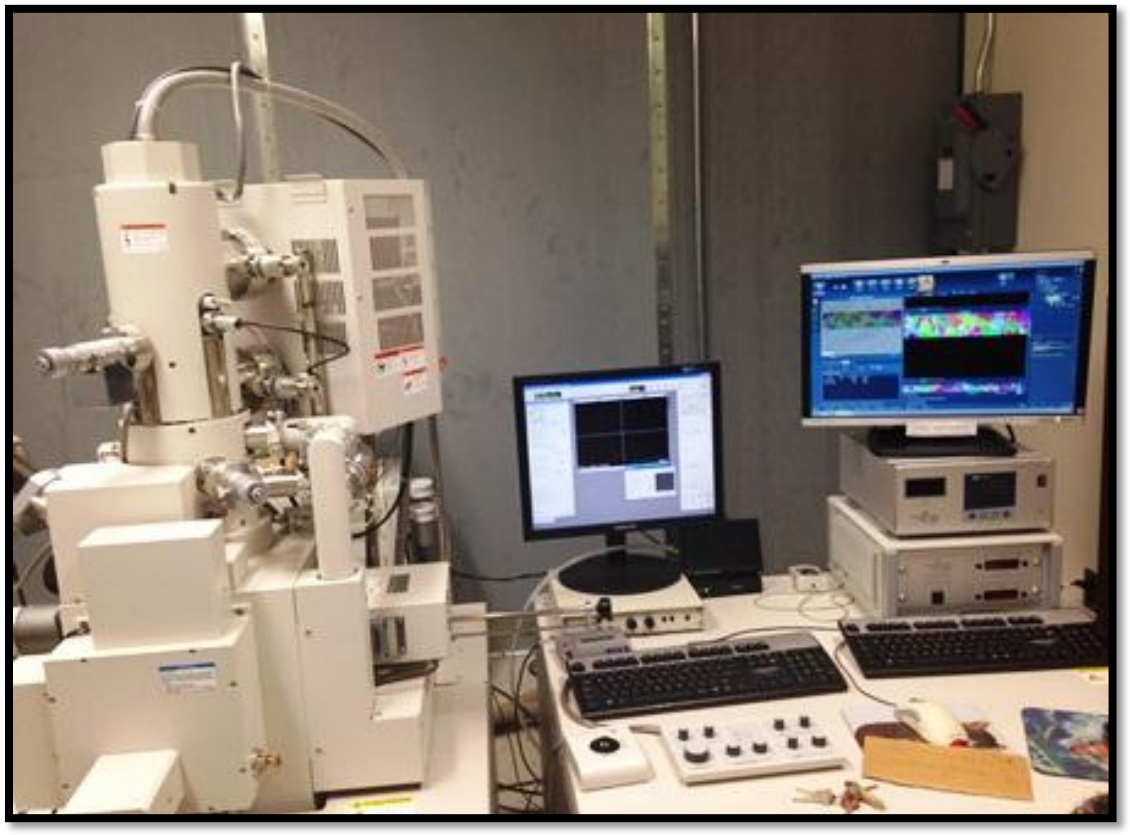


Figure 3. 6. Hitachi SU6600 scanning electron microscope used in the present study.

3.8. Effect of urea and PGE on brine viscosity

Urea and the best frother from the results obtained in section 3.7 were selected for viscosity studies. A canon-fenske opaque viscometer was used to investigate the effect of urea or glycol on the viscosity of brine.

10 ml of urea or PGE was mixed with 100 mls of saturated brine at 15^{o}C. A pipette was used to draw the urea or PGE-saturated brine solution into the receiving reservoir of the viscometer. In

one arm of the viscometer is a vertical section of precise narrow bore (the capillary). Urea/PGE-saturated brine solution was then drawn into the upper bulb by suction, and then allowed to flow down through the capillary into the lower bulb. The two etched lines indicate a known volume. The time taken for the level of the solution to pass between these marks is proportional to the kinematic viscosity. The experiment was repeated for saturated brine solution in the absence of additives.

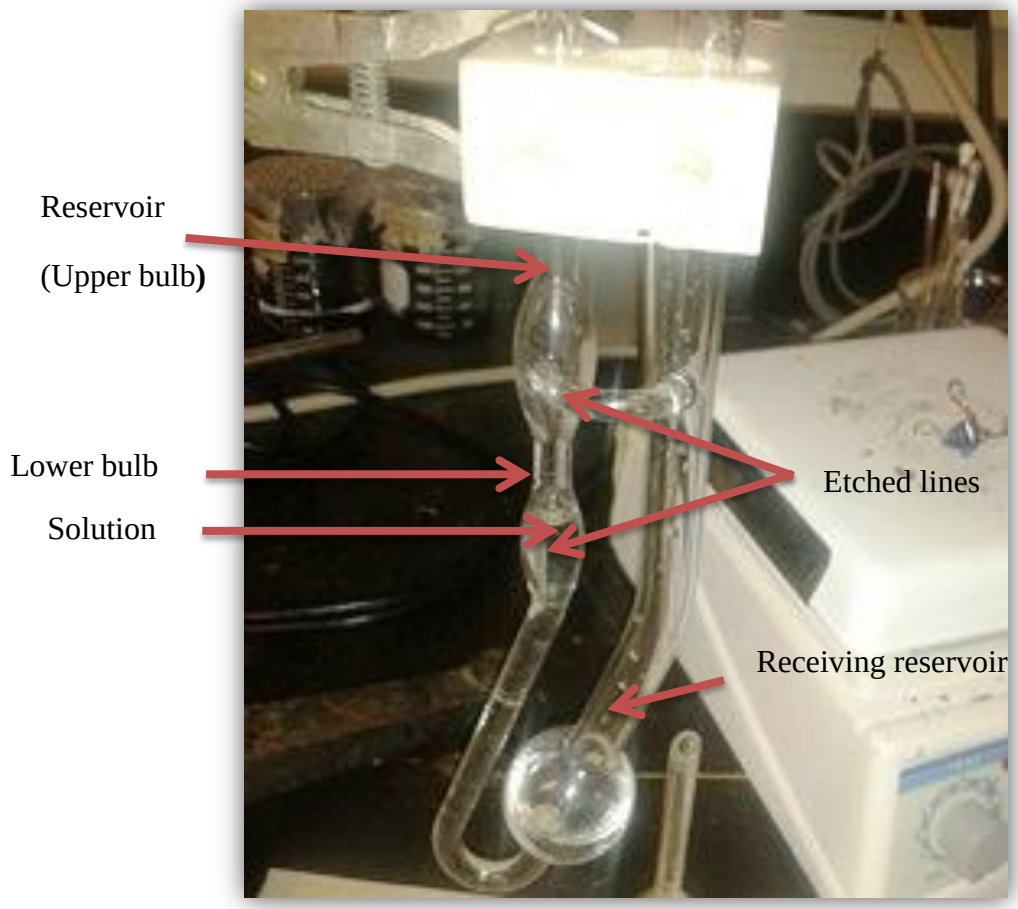


Figure 3. 7. Setup for viscosity experiment using canon-fenske viscometer.

3.9. Effect of PGE addition on amine adsorption on KCl

10 ml of 1 wt. % amine emulsion (without PGE) was pipetted into 100 ml beaker containing 50 ml of about 10^{o}C saturated brine. 5 g of pure KCl (3 pieces) was added to the resulting solution and gently stirred with a magnetic stirrer for 30 minutes to allow the amines to get attached (physisorption) to the KCl. The loaded KCl particles were picked out using a pair of tweezers

and stored in desiccators overnight to dry. The temperature measured after the experiment was 12 ± 2^{o}C. The experiment was repeated using 1 wt.% emulsion prepared by mixing amine (DDA-HCl) with PGE. The objective was to know the effect that mixing PGE will have on adsorption of amine on potash particles. 5 ml sample of the solution after adsorption (in each case) was pipetted into a beaker and 1 ml of acidified bromocresol green, a complexing agent was added to react for 5 minutes. After reaction, the resulting solution was transferred into a vial and 5 ml of chloroform was added. The mixture was shaken vigorously for about 30 seconds and allowed to stand undisturbed until two phases (organic phase and liquid `phase) were observed. The organic phase which is supposed to be a complex of amine and bromocresol green was extracted and the amine content remaining after adsorption was analyzed using a varain cary 100 scan U.V visible spectrophotometer located in the Thorvaldson building.

3.10 Flotation of KCl from low temperature and room temperature saturated brine

Flotation experiments were carried out using selected amine collector and organic additives from previous experiments. The flotation equipment used was an XFD laboratory flotation cell (Figure 3.5) equipped with a tank capacity of 3 l. The speed of the agitator was set at 1200 rpm (21.4 Hz) and the air flow rate was also set at 210 l/h. Flotation experiments were carried out at low temperature; 12 ± 2^{o}C or at room temperature 20 ± 2^{o}C and the pH of the brine was maintained at 6.5 ± 0.2. The aim of this experiment was to verify if results from the adsorption and dispersion tests could translate into better flotation efficiency. 750 g of sylvinite ore was poured into the flotation cell and 2.5l of saturated brine was added to form a pulp of 23% solids calculated as follows;

$$\%\ \text{Solids} = \left(\frac{\text{Weight of solid ore}}{\text{Weight of ore} + \text{Weight of brine}}\right) \times 100\%$$

200 g/t, 95 g/t and 50 g/t of depressant (CMC), Collector (DDA-HCl) and frother (PGE) were respectively used for the flotation experiments. The speed of the agitator was set at 1200 rpm (21.4 Hz). The airflow was also set at 210 l/h and maintained like this throughout the experiment. This first three flotation experiments were carried out with saturated brine at about 25^{o}C. The floated portion of the potash, (i.e. the concentrate) and the potash remaining in the cell after flotation, (i.e. tailings) were decanted and dried in an electric furnace at 105^{o}C. The dried concentrates and tailings were crushed and pulverized before being weighed using a mass

balance. The flotation products were thoroughly mixed and about 0.5 g representative specimen of each were then analyzed for KCl and NaCl using the PANalytical Empyrean powder X-ray diffractometer with the same operating conditions as in section 3.3.

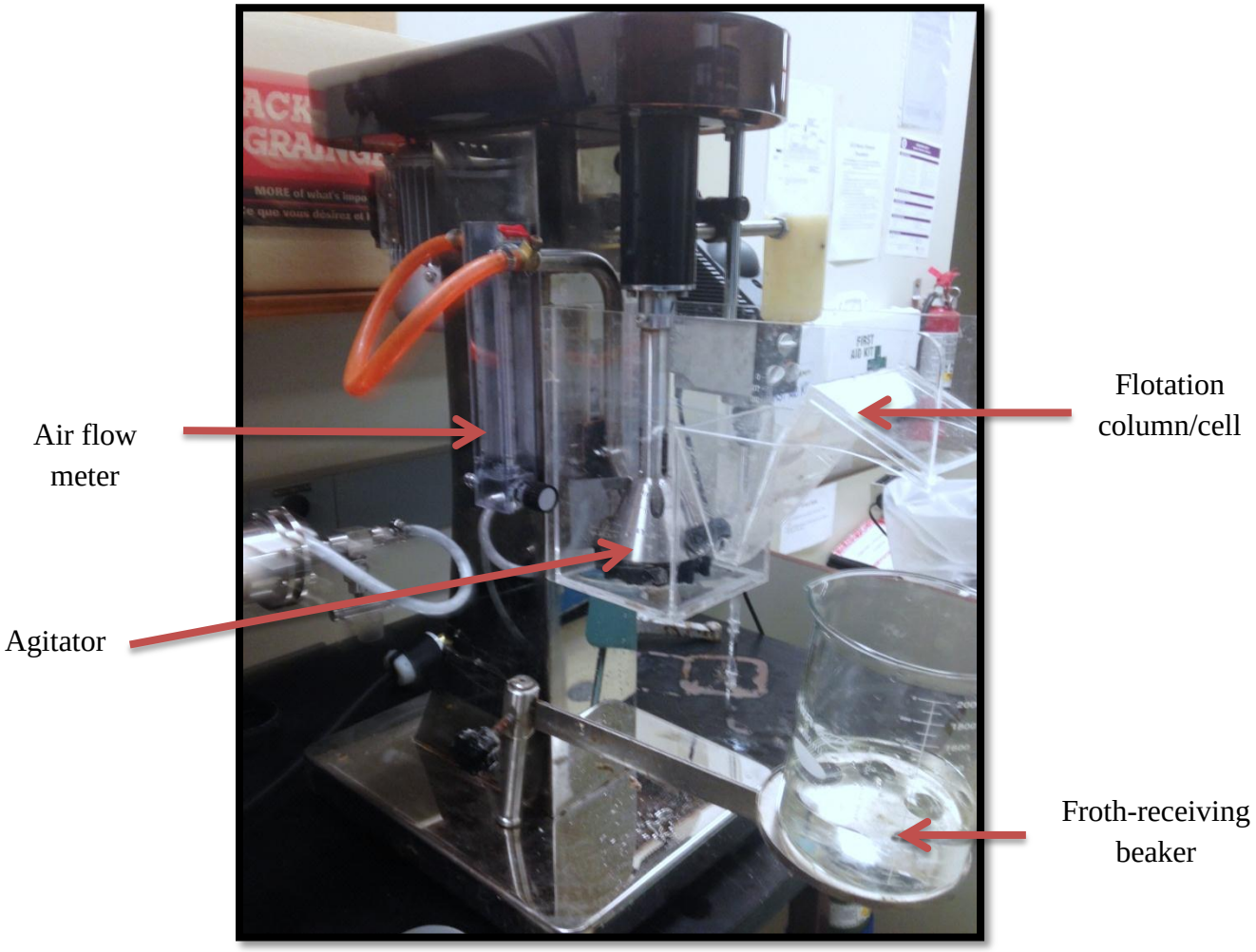


Figure 3. 8. Fu Xuan Dan-Cao (XFD) laboratory flotation apparatus.

Tube voltage 45 kV tube current, 40 mA, scan range 10 degrees to 80 degrees 2-theta step size 0.0167 degrees scan speed 0.0265 degrees/second. The percent weight of NaCl and insoluble matter accounted for the percent weight of tailings. The feed sample was also analyzed with the XRD to determine the initial compositions of the various components. Size analysis was done on the other fractions of the flotation product using sieves to determine the optimum particle size of potash. Using the assay values, flotation recoveries for each flotation test were then computed using a spread sheet.

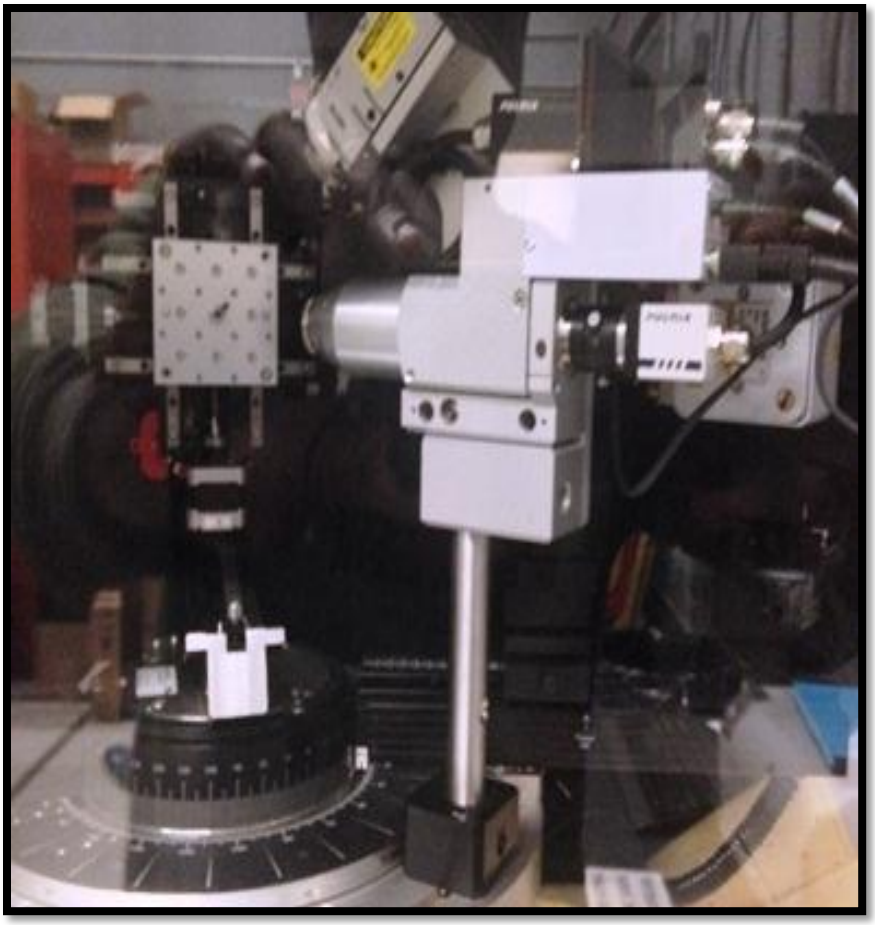


Figure 3. 9. PANalytical™ empyrean powder X-ray diffractometer.

3.10.1. Preparation of brine

The brine was prepared by pouring a sufficient amount of fine sylvinite (-180 µm) in deionized water. It was then agitated using a mechanical stirrer until the addition of more potash could not dissolve after 24 h of stirring. At this point the brine was saturated and was stored in storage containers. The density was measured to be 1.45×10^3 kg/m^3 and checked regularly before each experiment to ensure the saturation level was maintained.

3.10.2. Preparation of modified amine collector

Based on results from section 3.4.1, DDA-HCl was selected as the best long chain primary amine to be used for the preparation of a collector. PGE was selected as the best additive based on results from sections 3.6, 3.7, 3.8 and 3.9. First, 1 wt. % amine collector was prepared using the

same procedure as explained in section 3.1.1. PGE was then mixed with the hot fleshly prepared amine solution in a 1:1 ratio and mildly stirred for 120 seconds.

3.10.3. Recovery of KCl

Three flotation experiments were carried out to determine how temperature and the modify amine collector affect recovery of KCl.

In the first experiment, the collector used was a modified amine collector. The pulp was conditioned by the addition of depressant and the modified amine collector (mixture of amine and PGE in the ratio of 1:1) for 1 minute and then the frother was added. As flotation began, the floated KCl concentrate was skimmed off into the receiving beaker. Figure 3.10 is a flow diagram of KCl flotation with a modified collector.

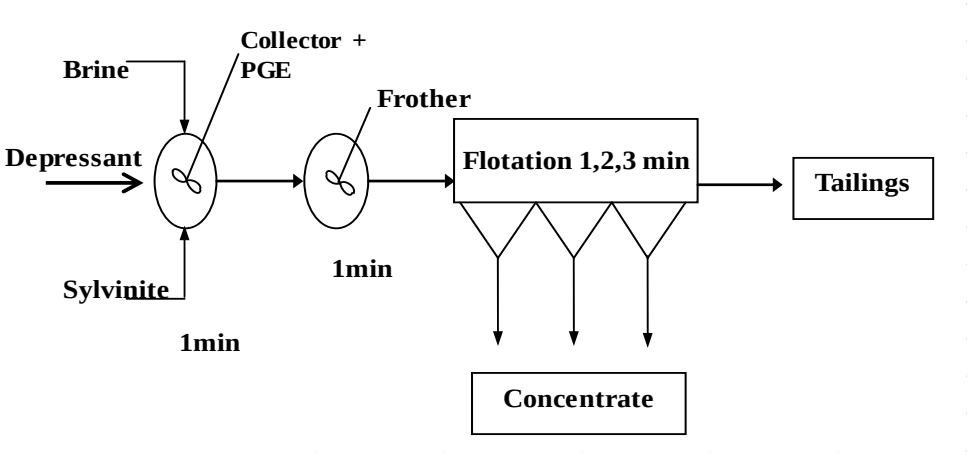


Figure 3. 10. Flotation with modified collector.

The purpose of the second experiment was to determine the effect of the absence of frother on flotation recovery. The pulp was conditioned by the addition of the modified collector and the depressant just like in experiment 1. However, there was no addition of a frother in this experiment as the PGE used in the modification of the amine collector was enough to function as a frother (See Figure 3.11).

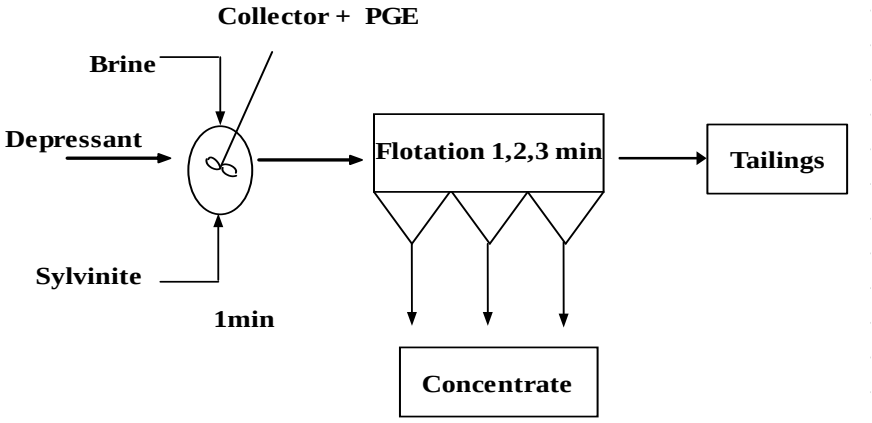


Figure 3. 11. Flotation with modified collector in the absence of a frother.

The third flotation experiment followed the conventional order of flotation experiments. It was used as the control for the first two experiments. The pulp was conditioned with the depressant and amine collector. The frother was then added and then flotation of the KCl began. Figure 3.12 is the flow diagram used for this experiment.

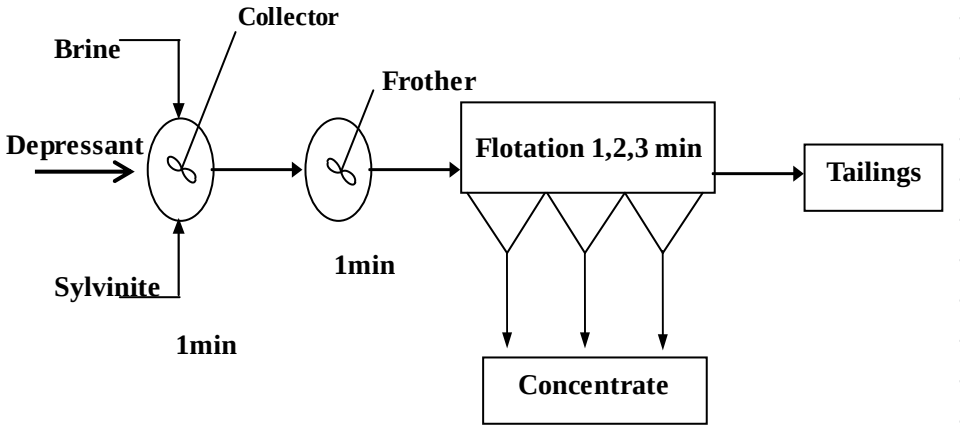


Figure 3. 12. Conventional flotation process.

3.10.4. Effect of the presence of urea on flotation recovery

In this study, three flotation experiments performed at room temperature and at low temperature to determine the effect of urea on flotation at low temperature. Figure 3.13 shows the flow diagram of these experiments. The temperature of the brine in the first experiment in this section (Experiment 4) was 24 ± 5^{o}C. The last two experiments (experiment 5 and 6) were performed using brine at 10-15^{o}C in the presence and absence of urea.

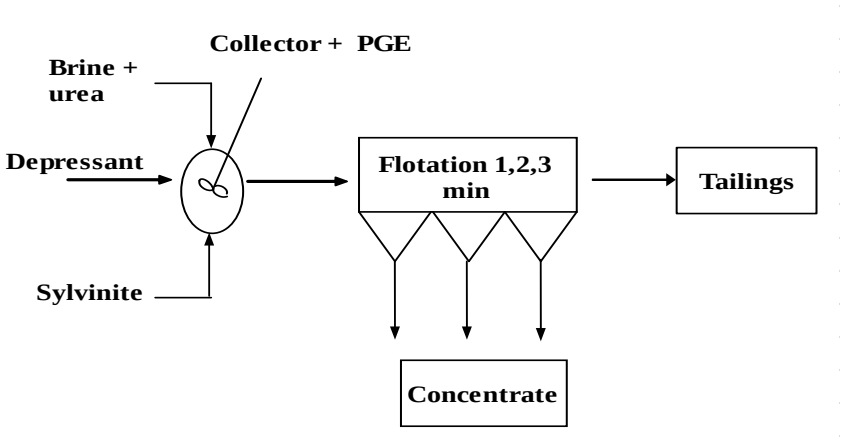


Figure 3. 13. Effect of urea on low temperature flotation.

3.10.5 Determination of flotation recovery

Flotation recoveries from conventional flotation processes were determined and compared with recoveries from flotation with modified collector and the difference was calculated to determine % change in recovery. % recovery is the percentage of KCl in the original feed that was recovered in the concentrate; calculated by using weights and assay values as;

$$R = (^{Cc}/_{Ff}) \times 100.$$

where

F = Weight of feed; C= Weight of concentrate; T= Weight of tailings; f= assay value of feed; c= assay value of concentrate; and t= assay value of tailings.

3.11. Determination of optimum particle size of floated KCl

Sieve analysis technique was used to determine the size range of the feed, and the dried and pulverized floated samples. Four different sieves (1.18 µm, 850 µm, 355 µm, 250 µm) were fitted on each other in ascending order of mesh sizes. The feed samples in batches were poured on the topmost sieve, 1.18 µm and covered. It was then placed on a shaker and shaken for 5 minutes to segregate the ore on the sieves. The quantity of ore in each sieve was weighed and recorded. The same process was repeated for the concentrate.

4. RESULTS AND DISCUSSION

4.1 Amine dispersion in saturated brine solution

The study of amine dispersion in saturated brine (sections 3.5 and 3.6) showed that the rate of dispersion of an amine depended on the alkyl group attached to the amine. The results from the dispersion tests are presented in Table 4.1. It was observed from the dispersion experiment that as soon as the amine collector was dropped into brine, the amine aggregates began to spread through the brine until it reached the other end of the container. As can be seen from Table 4.1, dodecylamine recorded the highest dispersion rate at both low and high temperatures. This can be explained by the fact that DDA has the smallest molecular weight compared to ODA and HDA. Therefore, it was selected as the candidate collector for subsequent experiments.

Table 4.1. Amine dispersion in saturated brine.

Alkyl amine	dispersion rate (mm/s) at 10 - 15^{o}C	dispersion rate (mm/s) at 20-32^{o}C
Dodecylamine Chloride	274	317
Octadecylamine Chloride	183	317
Hexadecylamine Chloride	153	312

4.2. Effect of temperature on amine precipitates

Figure 4.1 is an optical image of amine precipitates in saturated brine solution. The amine precipitates appeared to be translucent and the microscope seemed to have captured images of the shadows of the particles rather than the images of the amine particles. A careful look at Figure 4.1 can still tell that the amines are quite smaller in particle size and better dispersed in the brine at 26 ± 3^{o}C as compared to the size of amines in the 12 ± 3^{o}C brine solution. However, to be certain about this, scanning electron microscope (SEM) was used to observe the sizes and morphology of the amine precipitates; droplets of the samples were put on carbon tapes. Water in the samples were then allowed to dry before they were analyzed with the SEM. Figure 4.2 shows SEM images of DDA-HCl precipitates formed in saturated brine. It becomes clearer from this Figure that when amines are dispersed in cold saturated brine, the resulting amine precipitates

are bigger than when the brine is at temperatures at 26 ± 3^{o}C. (See Figure 4.2(a) and 4.2(b)). It was also observed that amine precipitates are poorly dispersed in low temperature brines. When there is poor amine dispersion in the flotation cell, attachment between KCl or air bubbles and amine particles is minimal and this can affect the recovery rate of KCl.

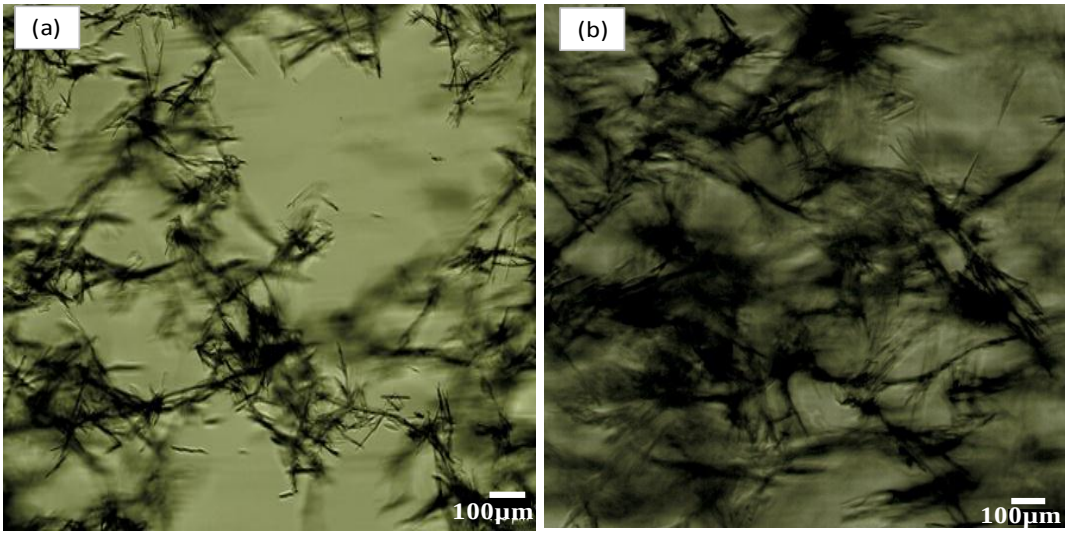


Figure 4. 1. Optical image of amine dispersion in brine: (a) at laboratory temperature, 26 ± 3oC and (b) at 12 ± 3oC.

.

In order to be sure that the SEM results showing larger amine particle sizes at low temperatures was not due to the particle coagulating on the copper tape as they spread, dynamic light scattering experiments were carried out. With this, the particle sizes of the amine precipitates were obtained while in saturated brine solutions under continuous stirring so it is not likely for coagulation to occur. Figure 4.3 is a graph of the particle diameter of amines verses the percentage volume of amine particles. It can be seen from Figure 4.3 that a higher volume of the amine precipitates in the brine maintained at 12 ± 3^{o}C were in the size range of 180-220 µm. In the case of amine precipitates in brine at 26 ± 3^{o}C, a higher volume of the amine precipitates were in the range of 40-50 µm. Thus, bigger amine precipitates form in saturated brines whose temperatures are relatively higher. This is an indication that spreading rate of amines at higher temperature is faster than spreading rate of amines at lower temperatures.

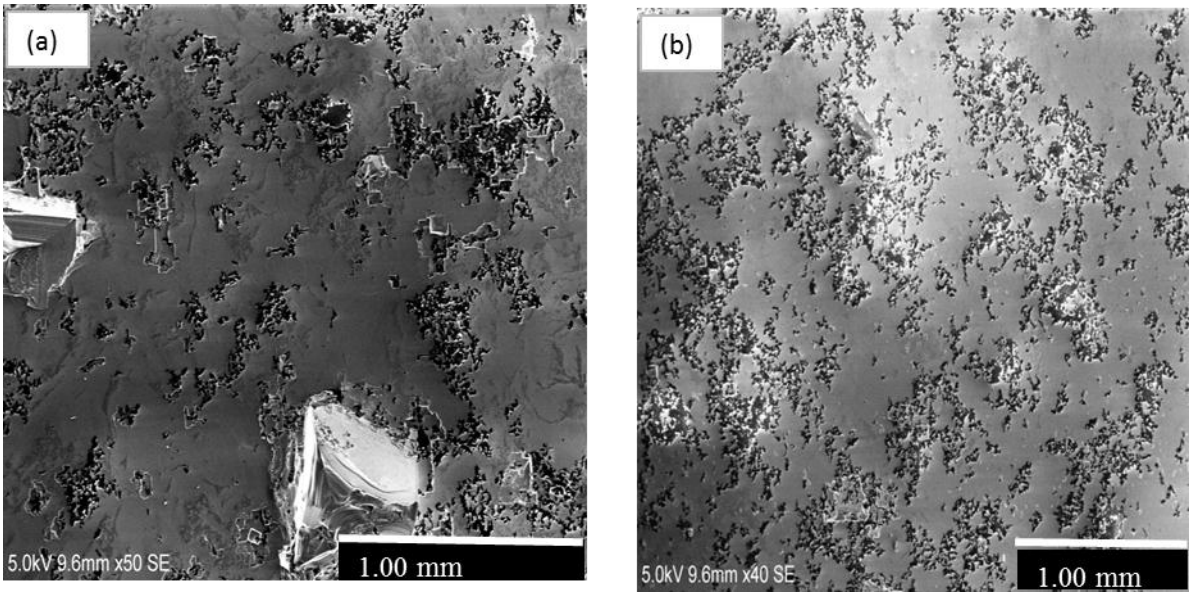


Figure 4. 2. SEM images of DDA-HCl precipitates formed in saturated brine: (a) at 12 ± 3oC and (b) at 26 ± 3oC.

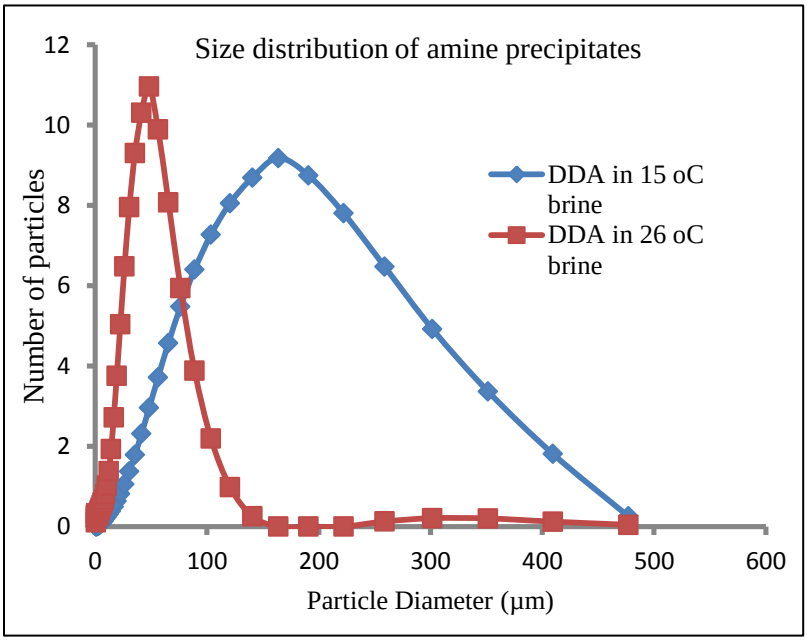


Figure 4. 3. Effect of temperature on amine dispersion using dynamic light scattering.

Generally, flotation with long chain primary amines like dodecylamine hydrochloride is carried out at room temperatures to about 32^{o}C to give a high potash recovery. Burdukova et al. (2009) showed that the particle size of amine dispersion is a function of the degree of amine dispersion which is a major contributing factor to efficient potash flotation. As shown in Figure 4.3, the

highest percentage of the amine dispersion in brine at 26 ± 3^{o}C was about 40 µm it is safe to state that for efficient flotation with amine, majority of the precipitates should have diameters not bigger than 40 µm.

With the knowledge that particle size of amine precipitates is critical for efficient flotation, with the size speculated to be about 40 µm, certain additives were mixed with the amine to determine their effect on size of precipitating amine dispersion. Figure 4.4 shows the effect of some selected additives (decanol, octanol and urea) on particle size of amine precipitates formed in saturated brine.

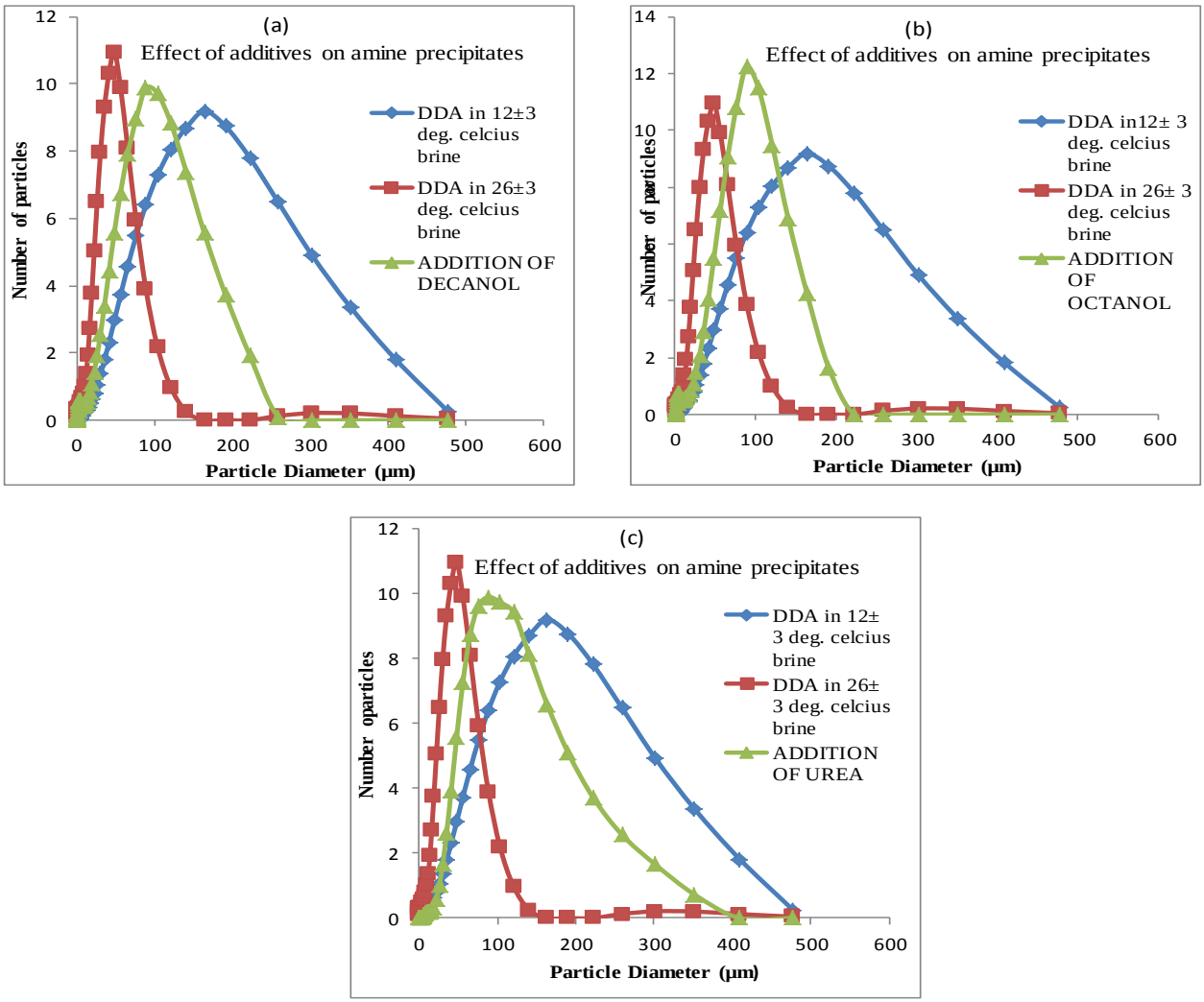


Figure 4. 4. Effect of: (a) decanol (b) octanol and (c) urea, on particle size of amine precipitates formed in saturated brine at 15^{o}C.

From Figures 4.4A, 4.4B, and 4.4C, it could be observed that the addition of all selected additives to brine solution maintained at 12 ± 3^{o}C produced a graph that got closer to the graph for the size range when the brine was kept at 26 ± 3^{o}C (red graph) and away from the blue graph (the size range formed when the brine solution was kept at 12 ± 3^{o}C. This means that in the presence of decanol, octanol and urea, the particle size of the amine (in cold brine) could be reduced to a size range close to that of the size range of amine formed from brine at 26 ± 3^{o}C temperature. Of the three additives, urea had the least impact. The other two additives were alcohols and their effect on particle size reduction was higher.

4.3. Effect of MIBC and PGE on particle size and dispersion of amine precipitates

It was found in section 4.2 that alcohols have a higher impact on particle size of amine precipitates. Also, it is known that most of the frothers (floatation reagent) used in potash flotation are alcohols. The two most popular frothers were then selected for further studies using the same dynamic scattering technique**.**

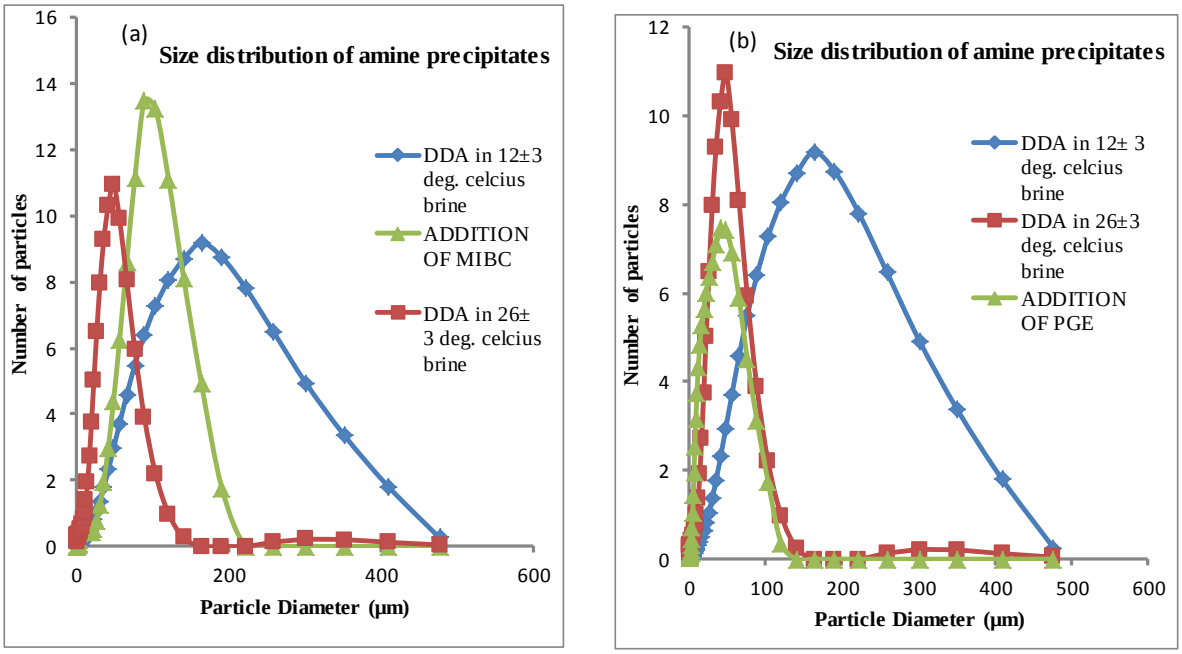


Figure 4. 5. (a) Effect of MIBC and (b) Effect of PGE on particle size of amine precipitates formed in saturated brine at 15^{o}C.

It was found from the graph (Figure 4.5) that by mixing the amine collector reagent with PGE or MIBC, the particle sizes in each case were significantly reduced to as close as possible to the

particle size range formed from brine at room temperature. This results and results obtained from the three additives were put together to find which graph drew farthest away from the graph for size range at 15^{o}C temperature. From Figure 4.6 it was clear that MIBC and PGE, the most useful flotation frothers, drew closest indicating that they had the highest impact on size reduction of the amine precipitates in saturated brine at low temperature (12 ± 3^{o}C).

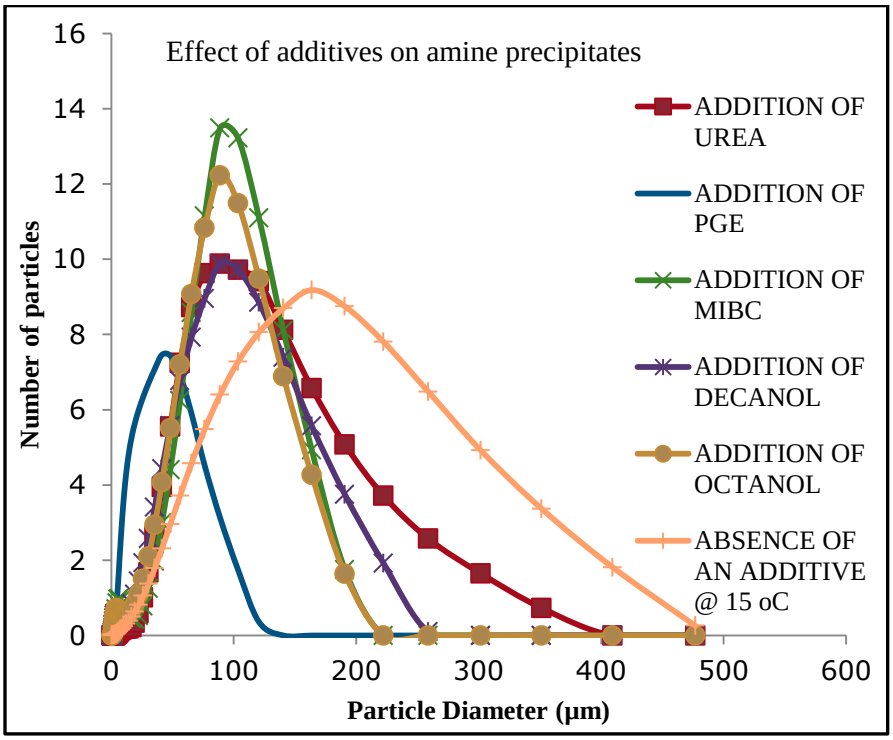


Figure 4. 6. Effect of additives, MIBC and PGE on size of amine precipitates.

4.4. Effect of MIBC and PGE on amine dispersion

Dynamic light scattering experiment on the amine particles showed positive results for MIBC and PGE. Further tests were done to find their effect on amine dispersion using SEM and OM. The SEM results from case 1 and case 2 represented by Figure 4.7 shows that mixing MIBC and PGE to the amine emulsions before addition to saturated brine influenced the morphology and size of the precipitating amine particles. In Figure 4.7(c) which depicts case 3 where no additive was added, it was clear that the amine precipitates were coarser and poorly dispersed on the surface of the polished KCl. Thus, amine precipitates are coarser when MIBC or PGE is not mixed with the emulsion during preparation of the amine collector. On the other hand, in Figures 4.7A and 4.7B, the precipitates spread all over the surface of the polished KCl, which is a good

indication of strong particle-amine attachment. This is helpful in improving bubble attachment and flotation efficiency.

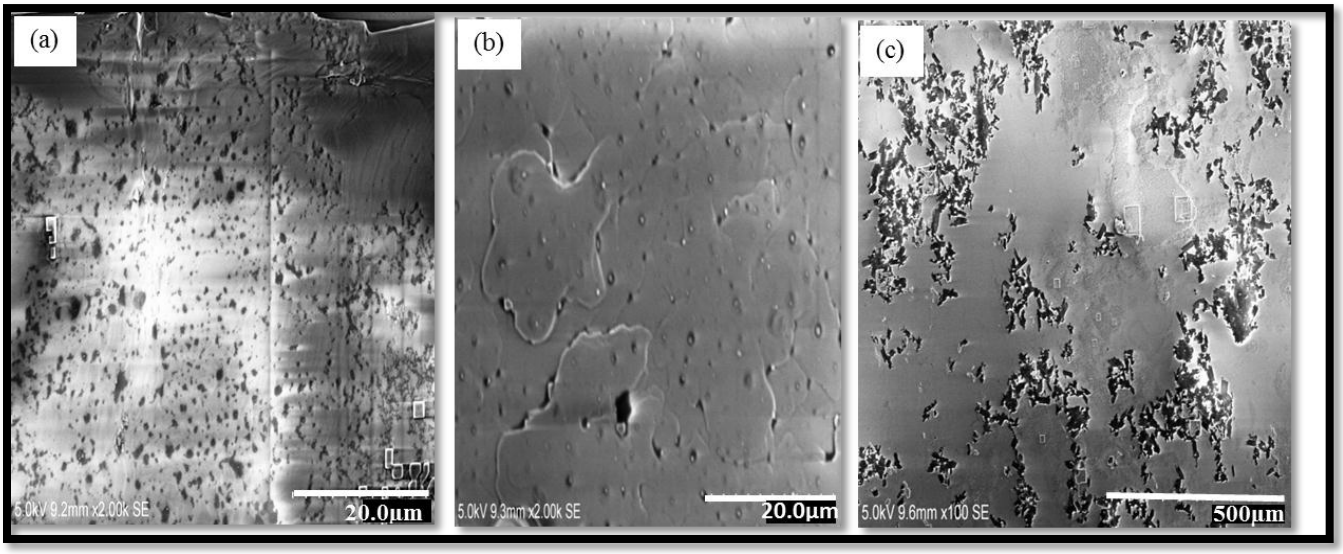


Figure 4. 7. SEM images of DDA particles (a) with MIBC present in the DDA emulsion, (b) with PGE present in the emulsion and (c) Without frother.

A repetition of the experiment using optical microscopy showed that the precipitates that were formed from amine emulsion in the absence of an additive had bigger diameters, an average diameter of 0.24 mm. Figure 4.8 is the optical images of polished KCl and DDA precipitates. It can be seen from the Figure that the diameters of the precipitates formed from amine emulsion that was prepared in the presence of MIBC and PGE were close to 0.1 mm. Different diameters of the precipitates were measured in each case and the average diameters were recorded to be 0.14 mm and 0.12 mm respectively for MIBC and PGE.

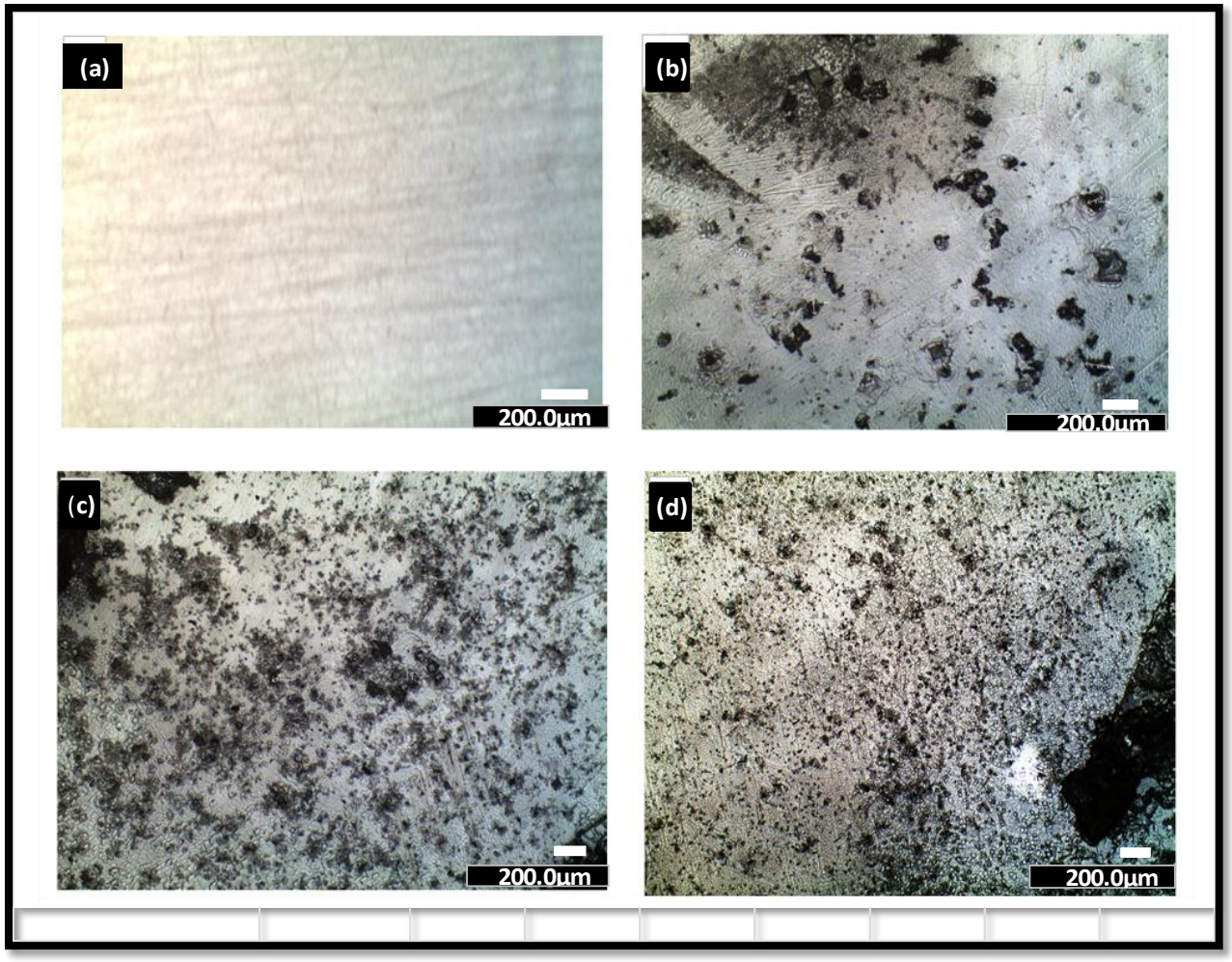


Figure 4. 8. OM images of (a) polished KCl surface (b) DDA precipitates in saturated brine without any additive present in the amine emulsion (c) with MIBC present in the amine emulsion, (d) with poly glycol ether present in the amine emulsion.

4.5. Viscosity test on organic additives

Canon-fenske viscometer was used to investigate the effect of additives (urea and glycol) on viscosity of brine. Based on the fact that MIBC is reported to have health issues, PGE was selected as the candidate frother for the viscosity studies. The selection of urea was based on literature, considering the fact that urea and its derivatives have been used to influence surface properties such as surface tension, viscosity and conductivity of liquids. Figure 4.9 is a graph of temperature verses relative viscosity of saturated brine solution prepared in the absence or in the presence of urea and PGE. From Figure 4.9 it is obvious that as brine temperature increases, the relative viscosity decreases. It was surprising to find from the results that in the presence of PGE,

the viscosity of the brine reduced by 7.28% as against urea which could only reduce the viscosity by 5.78% for temperatures at 15^{o}C (low temperature).

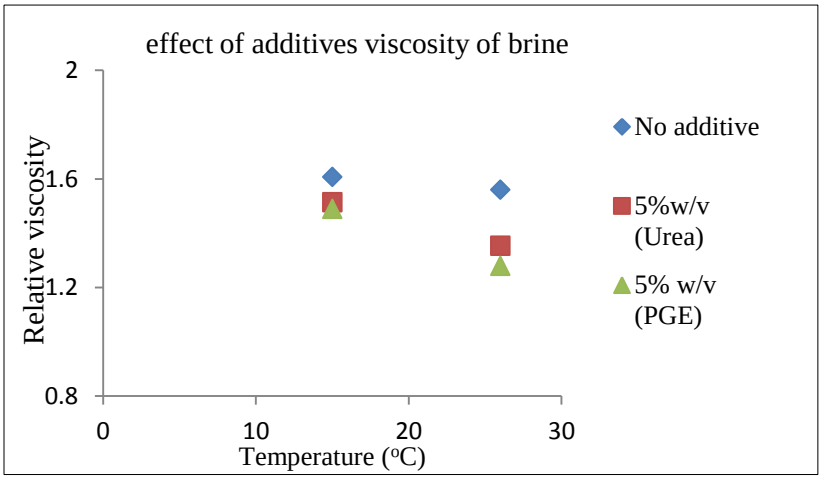


Figure 4. 9. Temperature verses relative viscosity of brine.

4.8. Effect of PGE on amine adsorption

The study of the effect of PGE on amine adsorption showed that some amine precipitates were adsorbed on KCl surfaces. Figure 4.10(a) and Figure 4.10 (b) show the results of the adsorption test. It can be seen from Figure 4.10(a) that KCl particles were trapped between DDA precipitates with attachment occurring at crystal edges. A similar observation was made by Qinbo et al. (2010) when they used molecular dynamic simulation to determine surface chemistry features of flotation with Octadecyl amine (ODA). Figure 4.10 (b) showed that the absorbance for the peak representing amine adsorption on KCl in the absence of PGE was higher than the peak for amine adsorption in the presence of PGE. This implies that in the presence of PGE, amine precipitates are able to attach or adsorb on KCl particles perhaps because of weakening of the bond between water molecules at the KCl surface and improvement of amine dispersion in the presence of PGE.

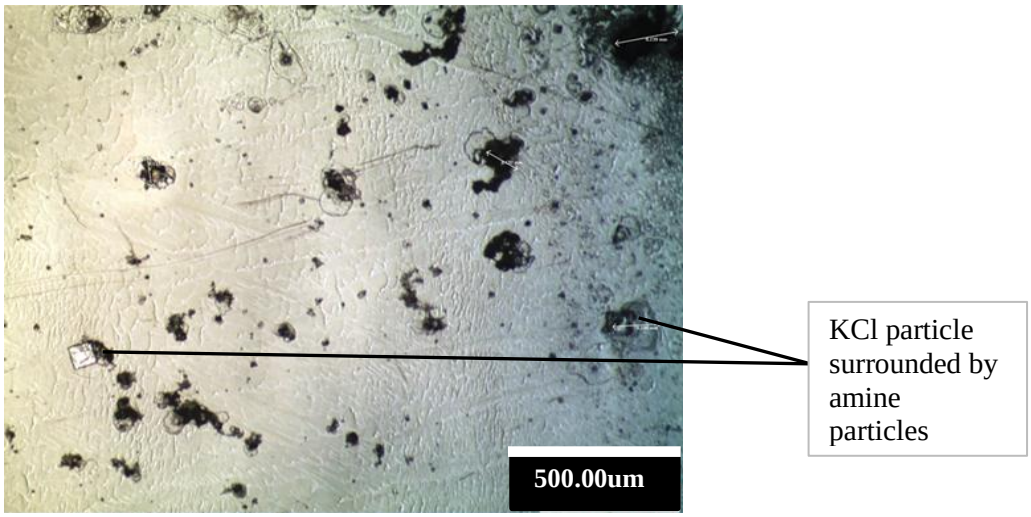


Figure 4. 10(a). Amine precipitates adsorbed on KCl particles.

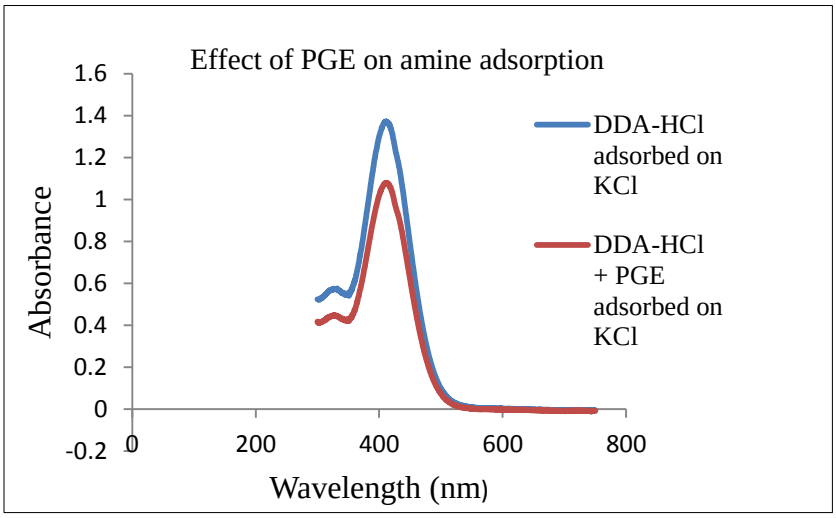


Figure 4.10(b) 1 Effect of PGE on amine adsorption by KCl

4.7. Effect of the use of modified collector (amine + PGE) on flotation recovery

The study of KCl flotation from saturated brine showed that the use of the modified amine collector and the way frothers were utilized in the flotation process had a significant effect on the percentage recovery of KCl. Different flotation results were obtained depending on the type of collector used (whether amine or modified amine collector) and whether or not a frother was added. The results are presented in Figure 4.11. In the first experiment the modified amine collector (mixture of DDA and PGE) was used. The sequence of reagent addition was;

depressant, modified collector and frother. In the second experiment, the order of reagent addition was; depressant followed by modified collector. There was no addition of a frother. Reagent addition in the third experiment followed the conventional depressant, amine collector, frother order. The collector used was a 'non-modified' (conventional amine collector). The third experiment was used as the control experiment.

Factors such as the agitation speed (as high as 1200rpm) and the aeration rate (as high as 210 l/hr) may have also contributed to the fairly good flotation results recorded. It was observed in experiment 1 that as soon as the modified collector (mixture of DDA and PGE) was added to the cell, frothing began. By the time the frother was added after 1 minute the cell began to over froth.

It can be read from Figure 4.11 that for each temperature condition; 23^{o}C, 25^{o}C and 28^{o}C, KCl recoveries in the second experiment (83.5%, 87.6% and 82.87%) were highest followed by recoveries obtained from the conventional flotation process in the third experiment (82.5%, 85.1% and 80.3%). Potash recoveries from the first experiment (79.3%, 75.6% and 78.5%), where modified amine collector was used in addition with the frother, were the lowest. This could be due to the effect of over-frothing which happens when too much frothing reagents are added into the flotation cell. Thus, the modified amine collector performed better than the non-modified collector and could significantly improve flotation recovery. Therefore it could be established that for improved recovery, the amine collector used should be modified with PGE and the flotation process should not include frother addition. Therefore, the order of reagent addition used in the second experiment was selected as the model flotation process for the next set of experiments.

The next set of flotation experiments were performed at low temperatures (10-15^{o}C) to determine the effect of the modified amine collector on low temperature flotation. Figure 4.12 shows the results for these experiments. Potash recovery from the conventional flotation process was 74.8%. When the modified amine was used, the recovery increased to 87.2% representing about 12% increase in recovery.

In another test, urea was added to the brine prior to the flotation process to determine how flotation recovery would be affected. Figure 4.12 showed that when urea was added to the 10-

15^{o}C saturated brine solution, the flotation recovery increased to 89.1%. This is about 1.9% increment which is a very significant improvement in recovery.

Flotation tests with the modified collector were repeated at a higher temperature (28^{o}C) to determine the effect of temperature on recovery. It could be shown from the results (Figure 4.12) that a higher recovery of 90.8% was recorded when the temperature of the saturated brine was maintained at 28^{o}C.

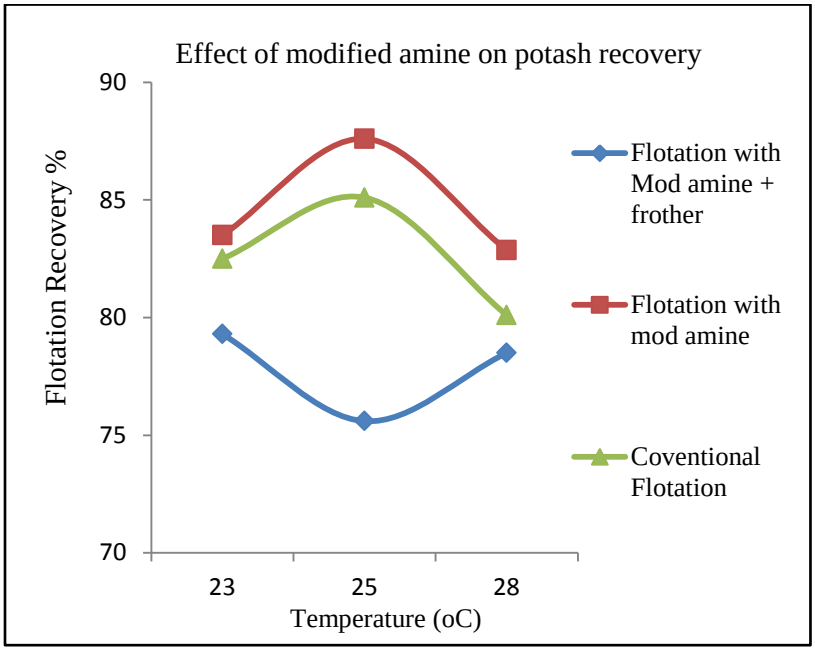


Figure 4. 11. Effect of modified amine (DDA+PGE) on flotation recovery.

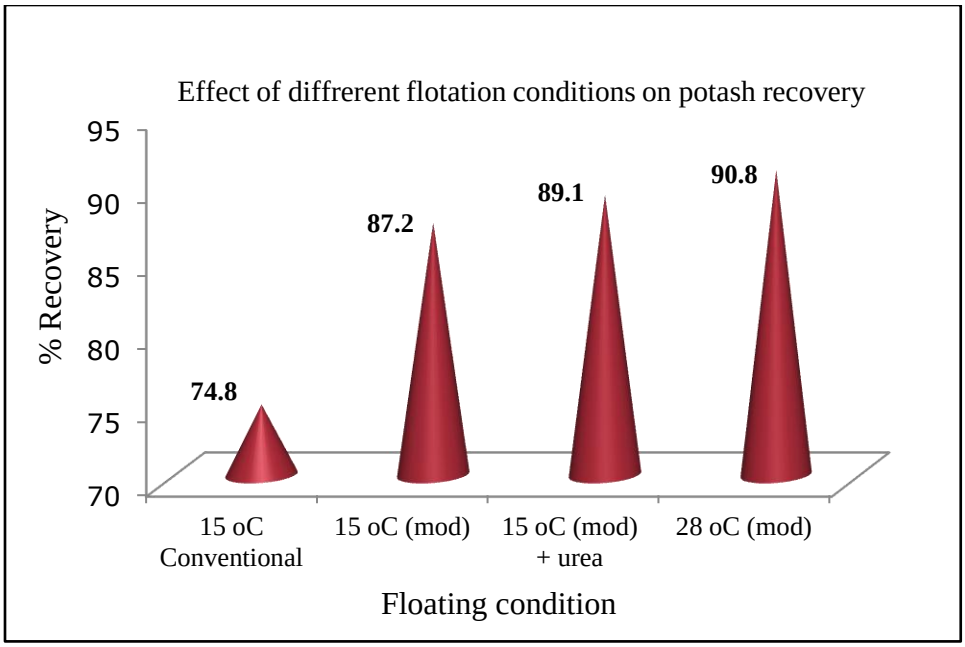


Figure 4. 12. KCl flotation from brines at 28oC and low temperature (15^{o}C).

4.9. Optimum particle size of potash particles

Results from the size analysis are shown in Table 4.4. It can be seen from the last column of the Table that 71% of the floated KCl particles were in the range of 180 µm and 335 µm representing the optimum particle size of potash that can be targeted during milling for efficient KCl flotation.

Table 4.2 Size distribution of potash particles.

Before flotation	**Feed % weight**	**Concentrate % weight**
-1.18mm, +850um	8	5.2
-850um, +335um	52	23
-335um, +180um	40	71.08

Error margin = ± 0.5

5. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1. Summary

This study showed that the flotation rate of KCl decreases with temperature as a result of reduction in the rate of transport of KCl from the bulk to the froth phase due to higher viscosity of the bulk solution (slurry). Thus, it can be explained that the bubbles carrying KCl particles rise more slowly at lower temperatures due to higher viscosities. However, in the presence of urea and PGE, viscosity of pulp is reduced and flotation recovery is improved. How urea and PGE reduces viscosity was not investigated. It was also shown that by mixing the collector with the frother (PGE) dispersion rate of amine increases, the particle size of amine dispersions reduces and flotation recovery is improved as a result. Thus, mixing the amine with the frother during preparation of the collector reagent improves recovery. It implies that the order of reagent addition for improved low temperature flotation is; depressant first, followed by the collector which in this case is the modified amine (mixture of PGE and DDA) as depicted by Figure 3.11. Thus, in order to obtain adequate KCl recoveries at lower temperatures, the brine solution can be mixed with urea and the order of reagent addition must not follow the conventional depressant, amine collector, frother order. The reagent addition must follow the order as represented by Figure 3.11.

5.2. Conclusions

1. From the flotation experiments carried out, it could be concluded that at lower temperatures (10-15^{o}C), the use of a modified amine collector (DDA-HCl + PGE) improved KCl recovery by 12%.
2. When urea was added to the brine, flotation with the modified collector further increased by 1.9%.
3. In the presence of the frother, flotation with the modified collector was very poor. Thus, flotation with the modified collector did not require the addition of a frother to the flotation system.
4. The optimum particles size required for improved flotation with the modified amine collector was 180-335 µm.

5.3. Recommendations

1. Further studies on the effect of temperature on surface tension of saturated brine and stability of air bubbles must be studied.
2. Effect of temperature and additives on contact angle should also be studied. This will help understand the other factors that could help in the improvement of flotation recovery.
3. Study of the interactions that occur between additives and saturated brine solution must also be studied to understand how viscosity is reduced in the presence of certain additives.
4. The formation of the amine precipitates in saturated brine should be studied further to find out how the precipitates are formed and how temperature and additives affect the particle sizes of the precipitates.

6. REFRENCES

Albrecht, T. Addai-Mensah J & Fornasiero, D. 2010. Effect of water temperature on sphalerite flotation. Chemeca proceedings: Engineering at the edge, ICMS, 2010.

Burdukova, E., Laskowski, J.S., 2009. Effect of insoluble amine on bubble surface on particle-bubble attachment in potash flotation. Can. J. Chem. Eng. 87, 441–447.

Burdukova, E., Laskowski, J.S. & Forbes, G.R. 2009. Precipitation of dodecyl amine in KCl-NaCl saturated brine and attachment of amine particles to KCl and NaCl surfaces, International Journal of Mineral Processing, 93, 34-40.

Bulatovic, S.M., 2007. Handbook of flotation reagents: Chemistry, Theory and Practice, 1, 1-51

Cao, Q., Du, H., Miller, J.D., Wang, X., Cheng, F., 2010. Surface chemistry features in the flotation of KCl. Miner. Eng. 23, 365–373.

Cao, Q., Wang, X., Miller, J.D., Cheng, F., Jiao, Y., 2011. Bubble attachment time and FITR analysis of water structure in the flotation of sylvite, bischofite and carnalite. Miner. Eng. 24, 108–114.

Dikhtievskaya, L.V. Osipova, E.O. Shevchuk, V.V. 2012. Increase in Flotation Activity of Salts of Higher Aliphatic Amines, Potassium Chloride Collectors, 85, 2011−2017.

El-Aila, H.J.Y. 2005. Effect of urea and salt on micelle formation of zwitterionic surfactants, Journal of Surfactants and Detergents 8, 165-168.

Forbes, E. Haihong Li, Bradshaw, D.J. & Franks, G.V. 2011. Poly (N-isopropylacrylamide) (PNIPAM) as a flotation collector: Effect of temperature and molecular weight, Minerals Engineering, 24, 772–777.

Fuerstenau D.W. & Fuerstenau, M.C. 1956. Ionic size in flotation collection of alkali halides. Min. Eng. 224, 302–307.

Gaudin, A.M., 1957. Flotation. McGraw-Hill, New York, 14. 295-304.

Garret, D.E. 1996. Potash: Deposits, Processing, Properties, and Uses: Chapman & Hall, 86

Gefvert, D.L. 1986. Cationic flotation reagents for mineral beneficiation, Chemical reagents in the mineral processing industry, D.M Malhatra-W.F. Riggs, eds., SME, 85-93.

Goldstein, A.M., Ater, E.N & Seaman, J.K. 1973. Guar gum, in Whistler, R.L. Industrial Gums, 2nd ed. Academic, New York, 14, 295-304.

Hancer, M. Miller, J.D., 2000. The Flotation Chemistry of Potassium Double Salts: Schoenite, Kainite, and Carnallite. Minerals Engineering, 13, 1483-1493.

Hancer, M., Celik, M.S., Miller, J.D., 2001. The significance of interfacial water structure in soluble salt flotation systems. J. Colloid Interf. Sci. 235, 150–161.

Kawatra, S.K., 2001. Froth Flotation – Fundamental Principles, Chemical Engineering, Michigan Tech.

Laskowski, J. & Kitchener, J.A. 1969. The hydrophilic to hydrophobic transition of silica, Journal of Colloid and Interface Science, 29, 670-679.

Laskowski, J.S. 2013. From amine molecules adsorption to amine precipitate transport by bubbles: A potash ore flotation mechanism, Minerals Engineering, 45, 170-179.

Leja, J.1983. On the action of long chain amines in potash flotation, Potash Technology: R.M McKercher, (Ed.), Pergamon Press, 623–629.

Leja, J., Schulman, J.H. 1954. Flotation theory: molecular interactions between frothers and collectors at solid-liquid-air interfaces. Trans. AIME 199, 221–228.

Lin, I.J. 1989. The effect of seasonal variations in temperature on performance of mineral processing plants, Minerals Engineering, 2, 190-196.

Miller, J.D., Yalamanchili, M.R. & Kellar, J.J. 1992. Surface charge of alkali halide particles as determined by Laser-Doppler electrophoresis. Langmuir 8, 1464–1469, 1992.

Miller J. D. & Yalamanchili, M.R. 1994. Minerals Engineering, 7, 305-317.

Monte, M.B.M. Oliveira, J.F. 2004. Flotation of sylvite with dodecylamine and the effect of added long chain alcohols. Minerals Engineering, 17, 425-430.

Navarrette, J., Johnson, J. & Gamble, J. 2006. Use of urea-formaldehyde resin in potash ore flotation, US Patent 2006/0226051 A1.

Newcombe, G. Ralston, J.1994. Bubble spreading kinetics and mineral flotation, Minerals Engineering, 7, 889–903.

O'Connor, C.T., Dunnet, R.C. & Botelho De Sousa, A.M.A. 1984. The effect of temperature on the flotation of pyrite, J. S. A fr. Inst. Min. Metal, 84, 389-394.

Ozdemir, O., Du, H., Karakashev, S.I., Nguyen, A.V., Celik, M.S., Miller, J.D., 2011. Understanding the role of ion interactions in soluble salt flotation with alkylammonium and alkylsulfate collectors. Adv. Colloid Interface Sci. 163, 1–22.

O'Brien, R.N., Visaisouk, S., Leja, J. A multiple surface balance use and results in selecting suitable flotation reagents. In: R.M McKercher, (Ed.). Potash Technology. Pergamon Press, pp.619–622, 1983.

Perucca, C.F. 2003. Potash processing in Saskatchewan: A review of process technologies. CIM Bulletin, Vol. 96, 61-65.

Perkins C.L. & Sayre, R. 1921. E. Flotation of minerals, United States Patent number 1364308,

R.L., BeMiller J.N., editors. Academic Press; New York: 1973. pp. 303–321.

Roman, R.J., Fuerstenau, M.C., Seidel, D.C., 1968. Mechanism of soluble salt flotation. Trans. AIME 241, 56–64.

Rogers, J. 1956. Flotation of soluble salts. Trans. IMM 66, 39–452.

Schubert, H., 1988. The mechanism of collector adsorption on salt-type minerals from solutions containing high electrolyte concentrations. Aufbereit.-Technik 29, 427–435.

Strathdee, G.G., Haryett, C.R., Douglas, C.A., Senior, M.V., Mitchell, J. 1982. The processing of potash ores by PCS: 14th International Mineral Processing Congress, Toronto, Paper no. V-12.

Titkov S., 2004. Flotation of water soluble mineral resources, International Mineral Processing, 74, 107-113.

Weedon, D. Grano, S., Akroyd, T., Goncalves K. & Moura, R. 2007. Effects of high Mg2+ concentration on KCl flotation: Part I - Laboratory research, Minerals Engineering, 20, 675–683.

Weedon, D. Grano, S., Akroyd, T., Goncalves, K. & Moura, R. 2007. Effects of high magnesium ion concentration on KCl flotation: Part II - Plant research, Minerals Engineering, 20, 716-721.

Wills, B.A. and Napier-Munn, T. J. 2006. Will's mineral processing technology, 7, 316-320.

Wilson, M., 1969. Method and means for beneficiating ores, US patent number 3424310.

7. APPENDICES

APPENDIX A: CALCULATIONS OF KCL RECOVERY

Feed:	750g	-1.18mm or -18 mesh Tyler Ore
Modifier/Depressant:	200g/t	Carboxymethyl Cellulose
Collector:	95g/t	Dodecyl amine
Frother:	50g/t	Polyglycol ether
Additive:	50g/t	Urea
Air:	210l/hr	
Impeller speed:	1200rpm	

	Sample weight (g)	Sample weight (%)	Assay (%) f,c,t			Recovery (%)
		F,C,T	KCl	NaCl	Insolubles	R
Feed	750	100	38	62	-	
EXPERIMENT 1						
Concentrate	270	36	79.8	18.2	2	75.6
Tailings	480	64	14	72	-	
EXPERIMENT 2						
Concentrate	277.5	37	90	9	1	87.6
Tailings	472.5	63	10	80.6	-	
EXPERIMENT 3						
Concentrate	288.5	38.5	84	16	-	85.1
Tailings	461.5	61.5	11.2	77	-	
EXPERIMENT 4						
Concentrate	284.2	37.9	91	6.5	-	90.8
Tailings	465.8	62.1	6	85	-	
EXPERIMENT 5						

Concentrate Tailings	270 480	36 64	92 8	7.5 75	- -	87.2
EXPERIMENT 6						
Concentrate Tailings	276 474	36.8 63	92 8.2	7.2 83	- -	89.1

Recovery is the percentage of the mineral of interest in the feed that is recovered in the concentrate.

$R = (^{Cc}/_{Ff}) \times 100$ Or $R = 100 \times (^{c}/_{f})(f - t)(c - t)$

Where F = Weight of feed

C= Weight of concentrate

T= Weight of tailings

f= assay value of feed

c= assay value of concentrate

t= assay value of tailings

Assay value is the quantity of KCl in a flotation material (feed, product or tailings)

EXPERIMENT 1

F= 100%; C= 36%; T= 64%

f= 38%; c= 79.8% t=14%

$R = [(36 \times 79.8)]/[(100 \times 38)] \times 100$

= 75.6%

Or by using only the assay values;

$$R = 100 \times (^{c}/_{f})(f - t)(c - t)$$

$$R = 100 \times (^{79.8}/_{38})(38 - 28)(79.8 - 14)$$

= 76%

APPENDIX B: DETERMINATION OF QUANTITY OF POTASH ORE TO USE

% Solids = 23%

Weight of slurry = 2.5kg

$$\% \text{ Solids} = (\frac{\text{Weight of solid ore}}{\text{Weight of slurry}}) \times 100\%$$

$$\% \text{ Solids} = (\frac{\text{Weight of solid ore}}{\text{Weight of ore} + \text{Weight of water}}) \times 100\%$$

Weight of solid used for flotation = x

Weight of brine to be added to ore to form 23% solids is calculated as;

$$23 = [\frac{x}{(x + 2.5)}] \times 100$$

$$100x = 23[x + 2.5]$$

100 x = 23x + 57.5

77 x = 57.5

x = 0.7467kg

$x \approx$ 750g.

APPENDIX C: DETERMINATION OF VOLUME OF FLOTATION REAGENTS TO USE

Data:

$$\text{Tonnage of potash ore used} = 750\text{g}$$

$$\text{Volume of reagent to be used} = \frac{(\text{Dossage of reagent} \times \text{tonnage of ore})}{\text{Concentration of reagent}}$$

Dossage of Depressant (CMC): 200g/t

Concentration of Depressant: 1% dispersion = 1g/ml = 0.01g/ml

$$\text{Volume of depressant used} = \frac{(200\text{g/t} \times 750\text{g})}{\frac{0.01\text{g}}{\text{ml}} \times 10^6}$$

$$= 15\text{ml}$$

Dossage of collector = 95g/t

Concentration = 1wt% = 0.01g/ml

$$\text{Volume of amine collector used} = \frac{(95\text{g/t} \times 750\text{g})}{\frac{0.01\text{g}}{\text{ml}} \times 10^6}$$

$$= 7.125\text{ml}$$

Dossage of Frother = 50g/t

Concentration=100%

$$\text{Volume of frother used} = \frac{(50\text{g/t} \times 750\text{g})}{\frac{1\text{ g}}{\text{ml}} \times 10^6}$$

$$= 0.0375\text{ml}$$

APPENDIX D: COPYRIGHT LETTERS

1. Figure 4.3 Images of DDA particles in a rapidly cooled suspension (A) with MIBC present in the DDA emulsion, (B) with MIBC present in the brine, (C) in the absence of MIBC (Burdukova et al, 2009).

ELSEVIER LICENSE

TERMS AND CONDITIONS

Jul 23, 2014

This is a License Agreement between Ebenezer Essilfie ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions. Supplier Elsevier Limited

The Boulevard, Langford Lane

Kidlington, Oxford, OX5 1GB, UK

Registered Company.

Number: 1982084

Customer name: Ebenezer Essilfie

Customer address: 301-107 Cumberland Avenue South, Saskatoon, SK S7N2R6.

License number: 3434921048652

License date: Jul 23, 2014

Licensed content publisher: Elsevier

Licensed content publication: International Journal of Mineral Processing

Licensed content title: Precipitation of dodecyl amine in KCl–NaCl saturated brine and attachment of amine particles to KCl and NaCl surfaces

Licensed content author: E. Burdukova, J.S. Laskowski, G.R. Forbes.

2. Figure 2. 0.1. The Saskatchewan Potash (www.canadapotash.com; Canada Potash Corporation, 2012)

We grant the permission to you for using the figure you attached to us on July 23 2014, with the only purpose of illustration of potash deposits in Saskatchewan in your thesis.

Best,

Junjie Liu

Geologist, Project leader, M. Sc. G.I.T

Canada Potash Corp.

200-402, 21St. E., Saskatoon, SK, S7K 0C3

Tel: 306-979-3700; Fax: 306-979-2773